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## The fate of river organic carbon in coastal areas: A study in the Rhône River delta using multiple isotopic ( $\delta^{13}\text{C}$ , $\Delta^{14}\text{C}$ ) and organic tracers

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### Abstract:

A significant fraction of the global carbon flux to the ocean occurs in River-dominated Ocean Margins (RiOMar) although large uncertainties remain in the cycle of organic matter (OM) in these systems. In particular, the OM sources and residence time have not been well clarified. Surface (0–1 cm) and sub-surface (3–4 cm) sediments and water column particles (bottom and intermediate depth) from the Rhône River delta system were collected in June 2005 and in April 2007 for a multi-proxy study. Lignin phenols, black carbon (BC), proto-kerogen/BC mixture, polycyclic aromatic hydrocarbons (PAHs), carbon stable isotope ( $\delta^{13}\text{C}_{\text{OC}}$ ), and radiocarbon measurements ( $\Delta^{14}\text{C}_{\text{OC}}$ ) were carried out to characterize the source of sedimentary organic material and to address degradation and transport processes. The bulk OM in the prodelta sediment appears to have a predominantly modern terrigenous origin with a significant contribution of modern vascular  $\text{C}_3$  plant detritus ( $\Delta^{14}\text{C}_{\text{OC}} = 27.9\text{‰}$ ,  $\delta^{13}\text{C}_{\text{OC}} = -27.4\text{‰}$ ). In contrast, the adjacent continental shelf, below the river plume, seems to be dominated by aged OM ( $\Delta^{14}\text{C}_{\text{OC}} = -400\text{‰}$ ,  $\delta^{13}\text{C}_{\text{OC}} = -24.2\text{‰}$ ), and shows no evidence of dilution and/or replacement by freshly produced marine carbon. Our data suggest an important contribution of black carbon (50% of OC) in the continental shelf sediments. Selective degradation processes occur along the main dispersal sediment system, promoting the loss of a modern terrestrial OM but also proto-kerogen-like OM. In addition, we hypothesize that during the transport across the shelf, a long term resuspension/deposition loop induces efficient long term degradation processes able to rework such refractory-like material until the OC is protected by the mineral matrix of particles.

## 66 1. INTRODUCTION

67 River-dominated Ocean Margins (RiOMar) play a critically-important role in the  
68 biogeochemical cycles of carbon, as they receive large amounts of riverine inputs of carbon  
69 and nutrients, sustaining large biological activity (Bianchi and Allison, 2009; Dagg et al.,  
70 2004; McKee et al., 2004). High rates of organic carbon (OC) burial and mineralization  
71 represent substantial sink and source terms in the carbon budget for the coastal ocean,  
72 providing insights on the underlying processes (Borges, 2005; Hedges, 1992). For instance,  
73 OC burial is the second largest atmospheric CO<sub>2</sub> sink and plays a major role in long-term  
74 climate regulation (Berner, 1990). Terrestrial OC (OC<sub>terr</sub>) originating from both continental  
75 erosion and river autochthonous production can be selectively degraded, deposited and buried  
76 in continental margins. The fraction of organic matter that escape either mineralization or  
77 burial in the shelf is then exported to the open ocean. OC burial efficiency in RiOMar areas is  
78 directly linked to the nature of terrestrial OC delivered to the coastal ocean because different  
79 origins and residence time ensure a wide range of reactivity (Hartnett et al., 1998; Hedges and  
80 Keil, 1995). Studying the structure, distributions and quantities of terrestrial organic matter, as  
81 well as processes governing its fate in the coastal ocean is a key for assessing global  
82 biogeochemical cycles (Galy et al., 2007; Raymond and Bauer, 2001a).

83 The Rhône River is the largest river input to the Mediterranean, both in term of water  
84 and particulate discharge rates (Ludwig et al., 2003), since the Nile River has been dammed.  
85 The Rhône River constitutes 80% of the total riverine inputs into the Gulf of Lions, the  
86 Northwestern Mediterranean continental margin, and provides  $1.6 \pm 0.5 \times 10^{10}$  mol C y<sup>-1</sup> to the  
87 Mediterranean Sea (Sempéré et al., 2000). In this context, the export and the fate of this  
88 terrestrial material from the Rhône River have been the subject of many intensive physical,  
89 biogeochemical and oceanographic studies (Estournel et al., 2001; Radakovitch et al., 1999b;

90 Roussiez et al., 2006; Tesi et al., 2007a; Ulses et al., 2008). These studies used radionuclide-  
91 based tracers that provided new insights into particle transfer processes although questions  
92 about the fate of river-borne organic matter still need to be addressed. Until recently, studies  
93 of particulate organic carbon cycling were mainly focused on off-shelf and canyon transfers  
94 rather than continental shelf distribution and margin processes (Tesi et al., 2010b). Thus,  
95 although the organic composition of the exported material was fairly well constrained in these  
96 studies, little insight is know about the chemical changes along the sediment transport in the  
97 shelf. Based on the results from Tesi et al (2007), Lansard et al (2009) made a first  
98 quantification of the terrigenous OC fractions of the Rhône River particles using stable  
99 carbon isotopes ( $\delta^{13}\text{C}$ ), C/N ratios and lignin-derived biomarkers. Their estimation relies on a  
100 two end-member mixing model between terrestrial and marine OC, and it is constrained by a  
101 narrow range of  $\delta^{13}\text{C}$  values. However, an approach like this can yield only a few information  
102 on the reactivity of the sedimentary OC.

103 To better understand the OM cycles in RiOMar systems and provide new insight about  
104 residence time and reactivity of sedimentary OC, additional tracers are required to estimate  
105 the contribution of terrestrial organic matter to continental margins and its fate. Radiocarbon  
106 values ( $\Delta^{14}\text{C}$ ), measured by accelerator mass spectrometry, have proven to be a powerful tool  
107 to investigate the dynamics of OC in river systems and marine environments (Druffel et al.,  
108 2005; Hedges et al., 1986a; Megens et al., 2001; Raymond and Bauer, 2001b). Radiocarbon  
109 can provide useful information on the sources and residence times of particulate organic  
110 matter (POM). Organic matter in river suspended particles presents a wide range of  $\Delta^{14}\text{C}$   
111 signatures from -980 to +75‰ (Blair et al., 2003; Druffel and Williams, 1991; Galy et al.,  
112 2007; Hedges et al., 1986b; Nagao et al., 2005; Raymond and Bauer, 2001a) whereas  
113 plankton and marine particulate organic carbon (POC) usually display enriched values from -  
114 45 to + 110‰ (Wang et al., 1998; Williams et al., 1992). Nevertheless, each river system

115 exhibits a contrasting range of  $\Delta^{14}\text{C}$  values of organic matter, reflecting both sediment  
116 transport processes within the watershed and local autochthonous production (Goni et al.,  
117 2006). This varying range of  $\Delta^{14}\text{C}$  values has been applied to distinguish sources of the  
118 deposited material (Blair et al., 2003; Goni et al., 1997). Furthermore, the combined use of  
119  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  adds a second dimension to assess the carbon cycling in river-dominated  
120 margins, especially to determine the fate and reactivity of particulate OC (Drenzek et al.,  
121 2007).

122 In this study, we used a multi-proxy approach on both sediments and suspended  
123 particles, combining  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  of bulk OC, lignin-derived biomarkers and their  
124 compound-specific  $\delta^{13}\text{C}$ , and polycyclic aromatic hydrocarbons (PAHs), black carbon (BC)  
125 and proto-kerogen/BC mixture, to elucidate the fate of terrestrial particulate organic matter  
126 released from the Rhône River to the Gulf of Lions continental margin. The chemical and  
127 isotopic analyses for these samples were modelled based on a four end-members model. The  
128 relative contributions of organic matter from various sources were quantitatively examined  
129 and the importance of pre-aged OC from continental shelf particles was demonstrated.

## 130 **2. BACKGROUND**

131 The Rhône River is the major source of freshwater, nutrients and organic carbon to the Gulf  
132 of Lions, a large continental shelf located in the NW Mediterranean Sea (De Madron et al.,  
133 2000; Pont et al., 2002; Sempéré et al., 2000). The Rhône River flows from the mountain  
134 range of the Alps to the Mediterranean Sea, where a delta is formed at its mouth. The  
135 catchment area of the Rhône River displays a strong climatic and geological heterogeneity  
136 since it drains oceanic, mountainous and Mediterranean weather systems over an area of 97  
137 800 km<sup>2</sup>. As an example of the catchment heterogeneity, part of the Durance River's basin  
138 (14 000 km<sup>2</sup>) is very rich in clay, devoid of vegetation and subjected to intense erosion

139 (Richy, 1992) when an important part of the Rhône River watershed consists of carbonate  
140 rocks (Pont et al., 2002). A consequence of such heterogeneity is a great variability in the  
141 hydrological regime of the Rhône River in terms of precipitation and solid transport capacity,  
142 with large differences between low ( $<700 \text{ m}^3 \text{ s}^{-1}$ ) and high ( $>3000 \text{ m}^3 \text{ s}^{-1}$ ) water -discharge  
143 rates (Pont et al., 2002). Most of the solid discharge is transported during Mediterranean  
144 floods but the mineralogical composition of the suspended matter reaching the river mouth is  
145 highly related to the flood origin (Ollivier et al., 2010; Pont et al., 2002). Similarly, the  
146 organic material exported at the Rhône River mouth derives from various allochthonous  
147 sources (vascular plants, bacteria and soils) and varies with flood events (Panagiotopoulos et  
148 al., 2012).

149 Large amount of terrestrial material is deposited in the sediments off the Rhône River mouth  
150 between 0 and 20 m water depth (Maillet et al., 2006). In fact, most of the material delivered  
151 by the Rhône River accumulates in the prograding prodelta (Fig.1) which extends from the  
152 shoreline to 60 m depth with a significant slope (Maillet et al., 2006; Wright and Friedrichs,  
153 2006). Net sedimentation rates in the prodelta range from 20 to 50  $\text{cm y}^{-1}$  at shallow stations  
154 (20 m) near the river mouth (Charmasson et al., 1998; Radakovitch et al., 1999a) down to  $\approx 1$   
155  $\text{cm y}^{-1}$  at 60 m water depth where the prodelta ends. The remainder of the Rhône River  
156 sediment delivered to the sea is transported and deposited onto the continental shelf at a mean  
157 rate  $< 0.3 \text{ cm yr}^{-1}$  (Miralles et al., 2005; Radakovitch et al., 1999a; Zuo et al., 1997).

158 The Northwestern Mediterranean current flowing southwestward along the slope imposes a  
159 general cyclonic circulation on the continental shelf of the Gulf of Lions (Fig. 1;(Milot,  
160 1990). Episodic southeasterly storms may cause the resuspension of Rhône River prodeltaic  
161 deposits that are then transported to the southwestern end of the shelf (Roussiez et al., 2005;  
162 Ulses et al., 2008). The Gulf of Lions is oligotrophic and the water column is seasonally

163 stratified. Intense vertical mixing events occur in winter and early spring due to strong  
164 regional winds and induce major nutrient export, through cascading and dense water  
165 formation (de Madron et al., 2003; Millot, 1990).

166 This study investigates the transition zone between the Rhône River prodelta and the Gulf of  
167 Lions continental shelf. Most of the changes in sedimentation rates happen within this zone  
168 subjected to resuspension (Fig. 1). We expect therefore significant changes in organic matter  
169 composition and new insights into the sediment transport system off the Rhône River mouth.

### 170 **3. MATERIAL AND METHODS**

#### 171 **3.1. Sampling**

##### 172 **3.1.1. River sampling**

173 Suspended particulate matter (SPM) from the Rhône River were sampled monthly from 2006-  
174 2009 at the Arles monitoring station (Maillet et al., 2006). The automatic sampler (CALYPSO  
175 2000S) is located 50 cm from the surface and 3 m from the bank, and the sampling is assumed  
176 to be representative of the entire water column due to the homogeneous SPM distribution  
177 along the cross and bottom-up section at moderate flow conditions (Pont et al., 2002). Four  
178 250-ml water samples were pumped per day into the same bottle, providing an integrated  
179 daily sample. For more details about the design and functioning of the monitoring station, see  
180 Pont et al (2002). River samples were collected every month over the course of the three  
181 years and covered a broad range of riverine discharge rates (Fig.1) including flood events.  
182 Water sub-samples were filtered in the laboratory on Whatman GF/F precombusted quartz  
183 filters in an all-glass filter holder and then dried for 24 h at 65°C and weighted to evaluate the  
184 total suspended particulate matter before further analysis (organic carbon and  $D^{14}C_{POC}$ ).  
185 Further analysis (organic carbon,  $\delta^{13}C_{POC}$  and  $\Delta^{14}C_{POC}$ ) were performed on freeze-dried

186 particulate material concentrated after a decantation step (24 h in a 5°C dark room) of the  
187 remaining water sample, following by a centrifugation (2000 rpm, 5°C, 5 min).

### 188 **3.1.2. Sediment and SPM Sampling**

189 Two scientific cruises (Minercot 2 and RiOMar 1) were conducted off the Rhône  
190 River mouth in June 2005 and April 2007, respectively. The network of sampling stations  
191 (Fig. 1) is described by Lansard et al. (2009) and the locations and water depths are displayed  
192 in Tables 1 and 2. The sampling strategy focused on the Rhône River prodelta, with a grid of  
193 closely spaced stations (A, B, K). The connection of the Rhône River prodelta with the  
194 continental shelf was studied through South-West, South and South-East onshore–offshore  
195 transects. The 2 cruises took place during period of average discharge rates of the Rhône  
196 River (Cathalot et al., 2010; Lansard et al., 2009).

197 Sediment samples were collected with a multicorer MUC 8/100 (Oktopus GmbH) deployed  
198 from the R.V. Téthys II. Eight cores (internal diameter: 9.5 cm) were simultaneously  
199 collected and sliced at 1 cm depth intervals. The subsampled sediments were then stored at -  
200 20°C until analysis. Sediment samples were freeze-dried and then ground using an agate  
201 mortar.

202 In addition, intermediate and bottom waters were collected using Niskin bottles in April 2007  
203 (Table 1). Water samples were filtered on Whatman GF/F precombusted quartz filters in an  
204 all-glass filter holder. Filters were washed with distilled water to eliminate the remaining salt  
205 and immediately frozen on board at -20°C. They were then dried at the laboratory for 24 h at  
206 65°C and weighted to evaluate the total suspended particulate matter.

### 207 **3.2. Organic Carbon Content**



208 Organic Carbon (OC) content was measured in surface sediment (0–1 cm) after inorganic  
209 carbon removal by dissolution with a 1% HCl solution. The OC content for the sediments  
210 collected in June 2005 were determined at LSCE, using an automatic Fisons Instrument NA  
211 1500 Element Analyzer, whereas OC measurements for the sediments sampled in April 2007  
212 were performed at CEFREM, by an automatic CHN-analyser LECO<sup>®</sup> 2000. Precisions for OC  
213 by both types of analyses were 2% (relative standard deviation).

214 Measurements of POC in bottom and intermediate waters (April 2007) were performed at  
215 LSCE using a different decarbonation treatment: filters were acidified with H<sub>3</sub>PO<sub>4</sub> (1%)  
216 during 24 hours at room temperature (Druffel et al., 1992). The remaining acid was removed  
217 by percolating through the filters, which were then dried at 65°C during two days. The  
218 precision for OC by this procedure was 3%.

### 219 **3.3. Stable Isotopic Composition of Organic Carbon**

220 Stable carbon isotope ratios of OC were determined in surface sediment ( $\delta^{13}\text{C}_{\text{OC}}$ ) and SPM  
221 ( $\delta^{13}\text{C}_{\text{POC}}$ ) after carbonate removal by acidification. Analysis of the June 2005 samples were  
222 performed using a continuous flow ThermoFinnigan Delta Plus XP Isotopic-Ratio Mass  
223 Spectrometer (IR-MS). Isotopic signatures of April 2007 sediments were measured at  
224 CEFREM on an Isoprime (GVI) IR-MS. An intercomparison between the two IRMSs was  
225 performed with 3 decarbonated samples from April 2007. Results showed no significant  
226 difference between the  $\delta^{13}\text{C}_{\text{OC}}$  values obtained ( $p < 0.01$ , non parametric Mann-Whitney test).

227 The isotopic compositions were reported using the standard  $\delta$ -notation (‰) with respect to the  
228 Vienna Pee Dee Belemnite (PDB) standard. Isotopic results were obtained with uncertainties  
229 of  $\pm 0.15\%$ .

230

### 231 **3.4. Proto-kerogen and Black Carbon fractionation:**

232 Two operationally defined pools of OC were chemically and physically isolated from bulk  
233 sediments. The wet procedure described by Song et al. (2002) was used to obtain a proto-  
234 kerogen/ black carbon (BC) mixture via acid demineralization, solvent extraction, and base  
235 hydrolysis. The procedure described by Gustafsson et al. (2001) was used to obtain pyrogenic  
236 BC through thermal oxidation and HCl treatment.

237 Description of the methods used to isolate and quantify the Proto-kerogen/BC mixture, and  
238 pyrogenic-graphitic BC are provided as Supplementary material.

### 240 **3.5. Polycyclic Aromatic Hydrocarbons (PAH) Analysis in the Rhône River Delta** 241 **Sediments**

242 The analysis of the Rhône River delta sediments included different suites of PAHs such as  
243 unsubstituted parent compounds, alkyl-substituted homologues (C-PAH) and unsubstituted  
244 sulfur heterocycle and their alkyl-substituted compounds (SPA<sub>H</sub> and C-SPA<sub>H</sub>). The  
245 concentrations were determined for more than 40 individual compounds and also group of  
246 their alkyl-substituted homologues (Tronczynski et al., 2004). A description of the method is  
247 provided as Supplementary material.

248 Quantitative PAH source apportionment was carried on the Rhône River samples together  
249 with PAH data determined in surface sediments from the bay of Biscay and the Northwestern  
250 Mediterranean Sea (Tronczynski et al., 2004). The source analysis in these sediment samples  
251 was constrained to two sources of PAH: i) pyrogenic/combustion, and ii) petroleum /oil  
252 residue. Two common mixture analysis approaches were adopted using Alternating Least  
253 Squares (ALS) and Multivariate Curve Resolution (MCR) calculation techniques (Larsen and  
254 Baker, 2003). Both methods give similar results ( $r^2 = 0.98$ ,  $n = 95$ ) and only ALS results are

255 presented here. Mixture analysis calculation provides PAH source amounts apportionment in  
256 each sample as well as PAH source profiles (compositions) estimates (Tauler et al., 1993).

### 257 **3.6. Lignin-Phenol Analysis**

258 A detail description of the method is provided in the Supplementary Material. Briefly, freeze-  
259 dried sediment samples (transect from station A to F) were analyzed for lignin-phenols using  
260 the cupric-oxide method (Hedges and Ertel, 1982). Lignin oxidation products were quantified  
261 by GC-FID.

262 We quantified eight lignin-derived phenols, unique to vascular plants, and produced during  
263 alkaline CuO oxidation. The vanillyl phenol (V) group, consisting of vanillin (Vl), vanillic  
264 acid (Vd) and acetovanillone (Vn), is present in all vascular plants. The syringyl group (S),  
265 consisting of syringaldehyde (Sl), syringic acid (Sd), and acetosyringone (Sn), are only found  
266 in woody and non-woody angiosperms. The cinnamyl phenols, ferulic acid (Fd) and *p*-  
267 coumaric acid (*p*-Cd), are only present in non-woody tissues of gymnosperms and  
268 angiosperms. In addition, CuO oxidation yields *p*-hydroxybenzenes (P) that are derived from  
269 both lignin and non-lignin sources (Goni and Hedges, 1995). Lignin parameters of total  
270 syringyl to vanillyl (S/V) and total cinnamyl to vanillyl (C/V) phenols were used to  
271 distinguish the relative contributions of plant types (gymnosperm vs. angiosperm) and tissue  
272 types (woody vs. non-woody) respectively. Cinnamyl phenols were found to be readily  
273 released from herbaceous tissues with a mild-base hydrolysis and exhibit a marked increase in  
274 lability relative to the lignin pool, during decomposition (Opsahl and Benner, 1994);  
275 therefore, to avoid the large variability in cinnamyl phenol pools and reactivity, the  
276 contribution of lignin to the organic matter pool was estimated using the carbon-normalized  
277 sum of syringyl and vanillyl phenols,  $\Lambda_6$  ( $\Lambda_6 = S + V$ ).

### 278 **3.7. Compound-specific Isotope Analysis of Lignin-Phenols**

279 The compound-specific  $\delta^{13}\text{C}$  values of lignin-derived phenols were measured by isotope ratio  
280 monitoring-gas chromatography-mass spectrometry (irm-GC-MS). Please see description in  
281 Supplementary Material. The  $\delta^{13}\text{C}$  value of the lignin pool was estimated by isotopic mass  
282 balance of syringyl and vanillyl phenols (equation 1):

$$283 \quad \delta^{13}\text{C}_{\text{S,V}} = \sum f_i \delta_i \quad (1)$$

284 where  $i$  represents individual lignin phenols (vanillin, vanillic acid, acetovanillone,  
285 syringaldehyde, syringic acid and acetosyringone);  $f_i$  represents the fraction of each phenol,  
286 and  $\delta_i$  indicates the  $\delta^{13}\text{C}$  value of the corresponding lignin phenol. Errors were calculated  
287 following the classical error propagation formula for the linear combination of each phenols  
288 contribution (equation 2):

$$289 \quad \text{std}\delta^{13}\text{C}_{\text{S,V}} = (\sum f_i^2 \text{std}\delta_i^2)^{1/2} \quad (2)$$

290 with  $\text{std}$  designating the error on the  $\delta^{13}\text{C}$  value considered.

291

### 292 **3.8. Radiocarbon Organic Carbon Content**

293 Radiocarbon measurements ( $^{14}\text{C}$ ) were performed either by the Artémis accelerator mass  
294 spectrometer (AMS) at the Laboratoire de Mesure du Carbone 14, Gif-sur-Yvette (for  
295 sediment samples) or by the NSF - Arizona AMS facility, Tucson (for suspended particles  
296 samples). Measurements were performed at two different sediment depths: 0-1 cm and 3-4 cm  
297 depth. After the decarbonation, the entire sample was combusted in a sealed quartz tube at  
298 850°C with copper oxide and silver wool. The released  $\text{CO}_2$  was dried, volumetrically  
299 measured, and collected in a glass ampoule. Then, the  $\text{CO}_2$  sample was converted to graphite  
300 target in an atmosphere of  $\text{H}_2$  over an iron powder catalyst at 600°C (Arnold et al., 1989) and

301 the sample  $^{14}\text{C}/^{12}\text{C}$  ratio was then measured. The  $^{14}\text{C}$  activities are determined with respect to  
302 the international standard of oxalic acid and are reported in  $\Delta^{14}\text{C}$  (Stuiver and Polach, 1977).  
303 The  $\Delta^{14}\text{C}$  is defined as the deviation in parts per mil from the modern standard. All  $\Delta^{14}\text{C}$   
304 values were corrected from 1950, and from the delay between sampling and measurement  
305 years (Mook and van der Plicht, 1999). Ages were calculated from the  $\Delta^{14}\text{C}$  values using the  
306 conventional  $^{14}\text{C}$  half-life. The precisions of  $\Delta^{14}\text{C}$  measurements were  $\pm 3\text{‰}$  for the sediment  
307 samples (Artemis AMS) and  $\pm 0.2\text{‰}$  for the suspended particles (Arizona AMS facility).  
308 Total uncertainties in  $\Delta^{14}\text{C}_{\text{OC}}$  are listed in Tables 1 and 2 for each samples.

## 309 **4. RESULTS:**

### 310 **4.1. River samples:**

311 The suspended particulate matter (SPM) sampled monthly from 2006 to 2009 in the Rhône  
312 River displayed a mean OC content of  $1.9 \pm 0.5 \%$ , and a  $\delta^{13}\text{C}_{\text{POC}}$  mean value of  $-27.4\text{‰} \pm$   
313  $0.7\text{‰}$  (Table 1). This  $\delta^{13}\text{C}_{\text{POC}}$  composition is in agreement with a previous survey on the SPM  
314 from the Rhône River, which gave a mean  $\delta^{13}\text{C}_{\text{POC}}$  of  $-26.8\text{‰} \pm 0.2\text{‰}$  over 2004-2005  
315 (Harmelin-Vivien et al., 2010; Harmelin-Vivien et al., 2008) and reflects the dominance of  
316 the  $\text{C}_3$  photosynthetic pathway within the Rhône River watershed throughout the seasons  
317 (Table 1).

318 Over the three years survey, SPM displayed  $\Delta^{14}\text{C}_{\text{POC}}$  signatures between 148 and  $-90\text{‰}$ ,  
319 including period of flood events. Black carbon (BC) contents in the Rhône River SPM were  
320  $0.34 \pm 0.12\%$  (d.w.).

### 321 **4.2. Background Data: Organic Carbon Content**

322 In April 2007, temperatures in bottom and intermediate waters were homogeneous over the  
323 entire study area (prodelta and continental shelf), ranging between  $14.1$  and  $15.3^\circ\text{C}$  at depths

324 of 13 to 98 m (Table 1). The SPM contents varied between 0.8 and 5.4 mg L<sup>-1</sup>, with no  
325 significant spatial pattern.

326 The highest POC concentrations were observed near the Rhône River mouth with values  
327 ranging between 150 and 266 µgC l<sup>-1</sup> (Stations A, K, B, L and N). The POC contents of SPM  
328 samples were around 10% at the river mouth and decreased offshore to values around 3%  
329 (Table 1). Surface and intermediate waters presented slightly higher POC contents than  
330 bottom waters, but given the variability, they were not significantly different (p>0.05).

331 The distribution and values of OC in surface sediment were stable over the two cruises  
332 and ranged between 2% at the vicinity of the river mouth and 1% offshore. The OC contents  
333 were slightly lower offshore during the June 2005 cruise but the overall prodelta distribution  
334 was not significantly different from April 2007 (p>0.05, Table 2, for data in June 2005 see  
335 Lansard et al, 2009).

### 336 **4.3. Stable Carbon Isotopic Composition**

337 The δ<sup>13</sup>C<sub>OC</sub> values for surface sediments collected in June 2005 are those reported by Lansard  
338 et al. (2009). The δ<sup>13</sup>C<sub>OC</sub> signatures did not show any significant changes between June 2005  
339 and April 2007 in surface sediment (p>0.05): values of δ<sup>13</sup>C<sub>OC</sub> ranged from -27.2‰ at station  
340 A (outlet of the river) to -23.9‰ at station J (south-eastward) (Table 2). All δ<sup>13</sup>C<sub>OC</sub> values  
341 increased with distance from the Rhône River mouth (r<sup>2</sup> = 0.845, n = 27, p<0.01, see Lansard  
342 et al., 2009). Stations A, B and K are located within a 2 km radius off the Rhône River mouth  
343 and presented strongly depleted δ<sup>13</sup>C<sub>OC</sub> values around -27 and -26‰, associated with high OC  
344 contents (~ 2%). Proceeding offshore, stable carbon isotope ratios rose up to -24‰ at the far  
345 most end of the South-West transect and eastern stations, corresponding to the lowest OC  
346 contents (~0.8 - 1%).

347 Contrary to surface sediment values, stable carbon isotope ratios of suspended POC ( $\delta^{13}\text{C}_{\text{POC}}$ )  
348 in bottom and intermediate waters were homogeneous in the whole prodelta, with values of -  
349  $24.0 \pm 0.3\text{‰}$  in bottom waters and  $-23.2 \pm 0.8\text{‰}$  in intermediate waters, respectively (Table  
350 1). There was no specific trend in spatial  $\delta^{13}\text{C}_{\text{POC}}$  distribution in the prodelta or the  
351 continental shelf.

#### 352 **4.4. Distribution of $\Delta^{14}\text{C}_{\text{OC}}$ and $\Delta^{14}\text{C}_{\text{POC}}$**

353  $\Delta^{14}\text{C}_{\text{POC}}$  signatures were measured in SPM from the Rhône River. Samples collected in April  
354 2006, March 2007, September and November 2008 and February 2009 displayed  $\Delta^{14}\text{C}_{\text{POC}}$   
355 values between  $-90\text{‰}$  and  $148\text{‰}$  (Table 1).

356 The  $\Delta^{14}\text{C}_{\text{OC}}$  signature of surface sediments in the prodelta presented a wide range of values  
357 from  $+143\text{‰}$  to  $-400\text{‰}$  (Table 2). A clear trend was observed with  $\Delta^{14}\text{C}_{\text{OC}}$  values decreasing  
358 with distance from the Rhône river mouth ( $r^2 = 0.942$ ,  $n = 14$ ,  $p < 0.01$ , see Fig. 2). Surface  
359 sediments in the immediate vicinity of the Rhône River mouth (station A) presented a modern  
360  $\Delta^{14}\text{C}_{\text{OC}}$  signature ranging between  $59\text{‰}$  and  $143\text{‰}$ , slightly higher than the current  
361 atmospheric  $\Delta^{14}\text{C}$ - $\text{CO}_2$  level ( $\sim 70\text{‰}$ , (Levin and Kromer, 2004)), and around  $0\text{‰}$  at B and K  
362 (Fig. 2, Table 2). Moving offshore, the  $\Delta^{14}\text{C}_{\text{OC}}$  signatures of sediments decreased rapidly with  
363 distance from the Rhône River mouth, down to values around  $-400\text{‰}$  in the most distal area,  
364 corresponding to an age of about 4000 years BP (Fig. 2; Table 2).

365 Except station A, which was markedly enriched with POC values in SPM of intermediate  
366 waters reaching modern carbon values, all stations showed SPM in bottom waters with  
367  $\Delta^{14}\text{C}_{\text{POC}}$  lower than  $-100\text{‰}$ . Offshore, the  $\Delta^{14}\text{C}_{\text{POC}}$  values of SPM decreased very quickly,  
368 down to values around  $-300\text{‰}$  (Table 1). At the station E, on the continental shelf, the  
369 radiocarbon signature of SPM ( $\Delta^{14}\text{C}_{\text{POC}}$ ) was similar to surface sediments  $\Delta^{14}\text{C}_{\text{OC}}$  (Table 1).

370 Nevertheless, our results show no correlation between sediment and overlying suspended  
371 POC radiocarbon signatures ( $p > 0.05$ , Table 1 and 2).

#### 372 **4.5. Black Carbon (BC) and Proto-kerogen/BC mixture:**

373 Sediment in the prodelta and the continental shelf display similar Black Carbon (BC)  
374 contents, ranging from 0.21 to 0.47% d.w. with a mean  $\delta^{13}\text{C}_{\text{OC}}$  value of  $-24.6 \pm 0.6\text{‰}$  (Fig. 6).  
375 Since OC content in the sediment decrease from the river mouth to the continental shelf (from  
376 1.8% to 0.8%), such constant BC values correspond to an increase from 12 to 50% of BC  
377 content in OC.

378 On the contrary, the proto-kerogen/BC mixture shows a clear decrease within the transition  
379 zone: sediment in the prodelta (stations A, B, K) displayed contents of  $0.69 \pm 0.12\%$  d.w.  
380 significantly higher than the stations on the continental shelf with values of  $0.47 \pm 0.02\%$ . In  
381 addition, the stable carbon isotopic signature of the proto-kerogen/BC mixture in the prodelta  
382 was  $-27.5 \pm 0.6\text{‰}$  whereas it was  $-25.3 \pm 0.4\text{‰}$  in the continental shelf. The proto-  
383 kerogen/BC mixture contribution to OC did not show any clear pattern over the area and was  
384 around 40-50% OC.

385 Please note that both fractions were obtained through different technique (chemical or thermal  
386 procedure) and the respective contribution of BC and proto-kerogen/BC mixture to OC  
387 content should not be compared among one another (Elmquist et al., 2004; Gelin et al.,  
388 2001).

#### 389 **4.6. Lignin-Derived Phenols And Their Stable Carbon Signatures**

390 The average carbon-normalized lignin contents ( $\Lambda_6$ ) were similar in the 1-2 cm and the 3-4  
391 cm depths and decreased with distance from the river mouth (Table 3). Syringyl and vanillyl  
392 phenol contributions were fairly equal (around 50%, Table 3) near the river mouth (station A)  
393 but the vanillyl phenol yield increased with offshore transport (Table 3), suggesting a greater



394 contribution of angiosperm tissues in near-shore sediments (Hedges and Mann, 1979b). The  
395 relative cinnamyl phenol yields were the lowest, ranging from 4.6% to 11.8% in upper 1-2 cm  
396 sediments and 5.6 to 7.2% at 3-4 cm depth. The S/V and C/V ratios at both depths generally  
397 decreased with an increased distance from the river mouth (Table 3, Fig. 3). The (Ad/Al)<sub>v</sub>  
398 ratio of sediments from the Rhône River transect did not significantly vary with offshore  
399 distance but nearly a doubling in (P/V+S) was observed (Table 3).

400  $\delta^{13}\text{C}$  values of the syringyl and vanillyl pool ( $\delta^{13}\text{C}_{\text{S,V}}$ ) were consistently lower in sediments at  
401 1-2 cm relative to those at 3-4 cm depth. However, there was an increase in the  $\delta^{13}\text{C}$  value  
402 along the transect at both depths (Table 3). From station A to station E, the  $\delta^{13}\text{C}$  value of  
403 lignin in surface sediments (1-2 cm) increased by 4.3‰, while those of sediments at 3-4 cm  
404 increased by 7.3‰ (Table 3). Despite its rather weak signigifance level (probably as a result  
405 of the low amount of data available), this increase in  $\delta^{13}\text{C}_{\text{S,V}}$  along the transect was  
406 statistically relevant ( $p \leq 0.1$ , Kruskal-Wallis).

#### 407 **4.7. PAH in the Rhône Prodelta And Adjacent Continental Shelf.**

408 Summed concentration of total PAHs in the sediment from the Rhône River prodelta and  
409 adjacent continental shelf ranged from about 2000 to 2400  $\mu\text{g kg}^{-1}$  (d.w.) and showed no  
410 gradient along the dispersal system (Table 4). Results from the Rhosos cruise performed in  
411 2008 (Tronczynski, unpublished results) were added as additional PAHs data in surface  
412 sediments of the continental shelf. The concentrations of total PAHs normalized to organic  
413 carbon ranged from about 110 to 330  $\text{mg kg}^{-1}$  OC and were higher at station C (75 m) than at  
414 the station A. The levels of summed sedimentary concentrations of six indicators  $\Sigma\text{PAH}_6$   
415 ranged from 450 to 600  $\mu\text{g kg}^{-1}$  d.w. (Table 4).

416 The petroleum component is estimated to be 30% (mean  $\pm 1$  %  $n = 4$ ) of total PAH in the  
417 Rhône delta sediments (Table 4) using mixture analysis calculation by ALS (Grande and

418 Manne, 2000). The remaining 70% originates from fossil fuel and biomass combustion  
419 (pyrogenic origin).

420 The total PAH content of the sediment was estimated by using a multiplying factor of 5 on  
421 our PAH estimates (Table 4) to account for all sulfur, oxygen and not quantified compounds,  
422 as previously used in coastal sediments (Tolosa et al., 1996; Tronczynski et al., 2004). The  
423 total PAH concentration in the Rhône River prodelta is thus about  $10 \text{ mg kg}^{-1}$  dry weight (dw)  
424 ( $2000 \text{ } \mu\text{g kg}^{-1}$  from Table 4 multiplied by 5).

425 Petroleum PAH fraction represents 30% of the total PAH (Table 4) which leads to a  
426 concentration of petroleum residues-PAH of  $3 \text{ mg kg}^{-1}$  dw. To calculate the petroleum carbon  
427 content, we used a conservative value of 20% of PAH in petroleum, since aromatic  
428 hydrocarbons significantly vary from one oil (and its refinery products) to another, ranging  
429 from 20 to 50% of different oils and refinery products (Lee et al., 1986). The total  
430 concentration of oil residue-derived OC in the sediment was therefore estimated to be  $15 \text{ mg}$   
431  $\text{kg}^{-1}$  dw ( $3 \text{ mg kg}^{-1}/20\%$ ).

432 The pyrogenic fraction of PAH is derived from combustion of fossil fuel or biomass and  
433 represents 70% of PAH : hence  $7 \text{ mg kg}^{-1}$  of PAH out of the total of  $10 \text{ mg kg}^{-1}$  was of  
434 pyrogenic origin (i.e. wood chars and soot). The predominance of fossil fuel combustion over  
435 residential wood combustion as the major source of pyrogenic BC and associated PAHs was  
436 examined by using ratios of 1,7-dimethylphenanthrene to 2,6-dimethylphenanthrene.  
437 Expressed as  $1,7/(1,7+2,6)$ -DMP, this ratio is known to be less than 0.42 for diesel particles  
438 and urban dust, whereas it reaches 0.70-0.90 in emissions from wood combustion (Benner et  
439 al., 1995). In sediment from our study area, we found this PAH ratio to be 0.45 implying that  
440 about 95% of the pyrolytic PAHs were derived from fossil fuel combustion (Yunker et al.,  
441 2012). Neglecting the wood/biomass combustion fraction, we can therefore consider that 7

442 mg kg<sup>-1</sup> of PAH out of the total of 10 mg kg<sup>-1</sup> originate from fossil fuel combustion (i.e. diesel  
443 soot, vehicle emission). In addition, assuming that PAHs represent 5% of the total combustion  
444 carbon (White et al., 2005), we can calculate a concentration of pyrogenic BC of 140 mg kg<sup>-1</sup>.

445

## 446 **5. DISCUSSION**

447 The radiocarbon signatures, stable carbon isotopic compositions and BC contents presented  
448 above indicate that different OC sources contribute to the organic matter in the river and shelf  
449 samples (Fig. 5). Additionally, lignin phenols' yields and isotopic signature suggest that a  
450 significant fraction of the organic matter exported by the Rhône River is lost during its  
451 introduction into the shelf environment. In the following sections, we investigate the sources  
452 of the OC pools exported by the Rhône River and the processes affecting their export in the  
453 sediments of the Gulf of Lions continental shelf.

### 454 **5.1. River input of organic matter: variability and signature**

455 The largest source of organic matter to the delta is the Rhône River which is  
456 characterized by large variations of discharge (Fig. 1). Flood periods, defined as water  
457 discharge rates exceeding 3000 m<sup>3</sup> s<sup>-1</sup> at Arles gauging station, occur in early spring and late  
458 fall and lasts from a few days to a week. These high discharge episodes are known to carry  
459 most of the material (about 80%) to the coastal ocean (Antonelli et al., 2004; Roussiez et al.,  
460 2005).

461 In this study, six periods characterized by high river discharge (with four floods) were  
462 investigated for  $\Delta^{14}\text{C}_{\text{POC}}$  whereas  $\delta^{13}\text{C}_{\text{POC}}$  was measured every month over the three-year  
463 study (January 2006 to February 2009). The time-series shows that the  $\delta^{13}\text{C}_{\text{POC}}$  signature of  
464 the suspended particles in the Rhône River is relatively stable ( $-27.4 \pm 0.7\text{‰}$ ) during both low

465 discharge and flood events (2006-2008). The Rhône River SPM displayed a variable  $\Delta^{14}\text{C}_{\text{POC}}$   
466 signature between 147 and -90‰ (average  $29 \pm 93\%$ ,  $n=5$ , Table 1) which likely reflected the  
467 mixing of different terrigenous materials in the River, i.e. fresh plant debris mixed with a low  
468 proportion of older soil organic matter. The  $\Delta^{14}\text{C}_{\text{POC}}$  signature of the Rhône River could also  
469 be influenced by the adjacent nuclear power plants: they can potentially increase the  $\Delta^{14}\text{C}_{\text{POC}}$   
470 signature in the river (Faurescu et al., 2008). This is contrasting with other RiOMar systems in  
471 temperate settings, where  $^{14}\text{C}$  signatures of POC are relatively older with  $\Delta^{14}\text{C}_{\text{POC}}$  signature  
472 ranging from -175‰ down to -550‰ (Raymond and Bauer, 2001a; Wakeham et al., 2009).  
473 The  $\Delta^{14}\text{C}_{\text{POC}}$  decreased to a low value of -495‰ only one time over the three years of  
474 monitoring, in May-June 2008, due to an exceptional flood of the Durance River located in  
475 the south-western Alps. This flood was linked to a water release by a dam. Therefore it is  
476 likely that during the event the flood wave carried a large amount of fine organic-poor  
477 sediments originating from bank erosion. This distinct source of organic matter was also  
478 obvious based on the  $\delta^{13}\text{C}_{\text{POC}}$  signature (-25.8‰), a value never reached during the 3-year  
479 monitoring period. On average, the organic matter supplied to the Rhône River prodelta  
480 corresponds to a modern terrestrial material similar to the one observed in the sediment of the  
481 shallowest station A located just off the river mouth (24 m water depth).

482

## 483 **5.2. The River-Shelf transition zone: major changes in particle signature**

484 The input of Rhône River exerts first order control on the composition of sedimentary  
485 organic matter located in the prodelta, i.e. near the river mouth. The terrestrial signature of the  
486 OM deposited in this zone is progressively altered along the sediment transport pathway  
487 along the continental shelf as shown on Fig. 4. We pooled our data with the ones from Tesi et  
488 al. (2007) and Tesi et al (2010a; 2010b) who had performed  $\delta^{13}\text{C}_{\text{OC}}$ ,  $\Delta^{14}\text{C}_{\text{OC}}$  and lignin

489 measurements in surface sediments further away in the Gulf of Lions continental shelf. The  
490 striking feature is the constancy of the particle signature on the entire shelf mud belt (Fig.4).  
491 Indeed, the  $\Delta^{14}\text{C}_{\text{OC}}$ ,  $\delta^{13}\text{C}_{\text{OC}}$  and OC contents presents less than 6% variation over a western  
492 125 km transect across the shelf. Regarding the biogeochemical parameters from this study,  
493 70% of the changes occur in the prodelta within a transition zone between the river mouth and  
494 the continental shelf. Most transformation, mixing, sorting and degradation processes  
495 altering/impacting the material delivered by the Rhône River appeared to occur within this  
496 narrow zone of 10 km radius area around the Rhône River mouth. On the contrary, shelf  
497 sediments display low organic carbon content, mixed  $\delta^{13}\text{C}_{\text{OC}}$  (-24.5‰) and low  $\Delta^{14}\text{C}_{\text{OC}}$   
498 (around -400‰) with a constant signature over the entire shelf of the Gulf of Lions. These  
499 sediments are characteristic of inert particles which are redistributed and mixed on the  
500 continental shelf by wind induced currents (Ulses et al., 2008; Estournel et al., 2003; Roussiez  
501 et al. 2006).

502 The transition zone displays a continuous gradient of isotopic signature (Fig. 4) with  
503 increasing distance from the Rhône River mouth. The shallow Rhône prodelta is a significant  
504 zone of retention for riverine particles, e.g. Station A (Table 2) which is located at 2 km from  
505 the river mouth at a depth of 24 meters. In addition to high sedimentation rates, it was shown  
506 using  $^{238}\text{Pu}$  that most particles delivered by the Rhône River were deposited and stored near  
507 the Rhône River mouth (Lansard et al., 2007). The isotopic composition of organic carbon in  
508 the sediment of station A reflects that of the river with a modern  $\Delta^{14}\text{C}_{\text{OC}}$  (+ 60-140‰) and a  
509  $\delta^{13}\text{C}_{\text{OC}}$  of -27‰. Furthermore, the large lignin content of the sediment suggests that the  
510 organic material is mostly terrestrial. Although this station exhibits the highest mineralization  
511 rate of organic matter in the sediment (Cathalot et al., 2010), it is mostly an accumulation  
512 centre with a burial efficiency of 80% (Pastor, Cathalot et al., 2011).

513 Stations located further away from the river mouth (B, K, L, N, C) in the transition  
514 zone (3-10 km) showed a progressive change of the primary signature of the river particles.  
515  $\Delta^{14}\text{C}_{\text{OC}}$  decreases to values as low as -220‰ at station C and  $\delta^{13}\text{C}_{\text{OC}}$  increases to -25‰,  
516 reflecting the apparent aging of organic carbon and its loss of terrestrial signature,  
517 respectively (Fig. 2, Table 2). In this region, several processes may modify the original  
518 signature of river particles: (1) selective degradation of relatively young terrestrial organic  
519 matter, (2) sorting of particles with different biogeochemical signatures (fossil versus labile  
520 carbon with different size/density characteristics (Tesi et al., 2007a), (3) mixing with the pool  
521 of old and refractory shelf particles. Mineralization rates are substantial in the sediment of the  
522 transition zone (Cathalot et al., 2010) and burial efficiency decreases from 60% (stations B,  
523 K, L) to 20% (station E) indicating that a substantial part of organic carbon is processed in  
524 these sediments (Pastor et al., 2011a).

525 In the next sections, we discuss the processes and their interplay which may lead to the  
526 observed isotopic and biomarkers gradient.

527

### 528 **5.3. Hydraulic sorting within the prodelta area**

529 Hydraulic transport mechanisms, which preferentially transport the finest material,  
530 alter the grain size distribution in surficial sediments (Marion et al., 2010). To assess the  
531 impact of grain size distribution on the export of OM in sediment of the Rhône River prodelta  
532 and the adjacent continental shelf, we plotted our radiocarbon signatures as a function of the  
533 silt/clay fraction content (Pastor et al., 2011b). Figure 7 clearly shows a dual behaviour of  
534  $\Delta^{14}\text{C}_{\text{OC}}$  signatures with respect to grain size distribution. In the prodelta, a clear gradient in  
535 the  $\Delta^{14}\text{C}_{\text{OC}}$  values suggest a loss of a young coarse material in the transition zone (stations A,  
536 B, K) as the sediment is being exported towards the continental shelf along the main sediment

537 transport system. This corresponds most likely, to a “fresh” woody material associated with  
538 coarse-sized particles preferentially retained close to the river mouth (Tesi et al., 2007a). As a  
539 consequence of this initial hydraulic sorting, soil-derived OM bound to the particles and all  
540 small size particles are selectively transported further offshore (Tesi et al., 2007a).

541 Soil OM can display a wide range of  $\Delta^{14}\text{C}_{\text{OC}}$  signatures ranging from modern to pre-  
542 aged values and has been proven to constitute a significant part of the sediment OM in many  
543 RiOMar systems (Hedges et al., 1999; Mannino and Harvey, 2000). Nevertheless, the  
544 sediment granulometry is homogeneous over the continental shelf (silt and clay < 63  $\mu\text{m}$   
545 fraction:  $95.3 \pm 1.0\%$ , Fig. 7) and the wide range of  $\Delta^{14}\text{C}_{\text{OC}}$  values (-102‰ to -400‰)  
546 suggesting a limited grain size sorting after the transition zone. The correlation between  
547  $\Delta^{14}\text{C}_{\text{OC}}$  and the particle size fraction < 63  $\mu\text{m}$  ( $r^2=0.730$ ,  $n=24$ , Fig. 7) disappears when  
548 considering only the continental shelf stations ( $r^2=0.024$ ,  $n=16$ , Fig. 7). Previous studies  
549 described the very fine sediment of the continental shelf, demonstrating the presence of an  
550 uniform fine-grained mudbank all over the continental shelf (except for littoral  
551 sands)(Lansard et al., 2007; Roussiez et al., 2006). As evidenced for other deltaic systems,  
552 particle sorting is likely to be responsible for the gradient of radiocarbon values observed in  
553 the transition zone by retaining some coarse woody particles in the shallow prodelta  
554 (Toussaint et al., accepted). However, over the continental shelf, this process might be of less  
555 importance and fails to explain the distribution of  $\Delta^{14}\text{C}_{\text{OC}}$  signatures over the continental  
556 shelf. Other mechanisms are likely acting along the main sediment transport system.

#### 557 **5.4. Contribution of ancient OC to the continental shelf sediment**

558 The surface sediments of the continental shelf displayed highly depleted  $\Delta^{14}\text{C}_{\text{OC}}$  values  
559 compared to the prodelta (Fig. 2, Table 2). Radiocarbon values in the continental shelf were  
560 about  $-310 \pm 66\%$ . [The residence time of the OM in the sediment cannot explain this low](#)  
561  [\$\Delta^{14}\text{C}\_{\text{OC}}\$  values.](#) Indeed, based on the published sedimentation rates (0.1-0.4  $\text{cm y}^{-1}$ ) and a 10

562 cm mixed layer (Miralles et al., 2005), the average  $\Delta^{14}\text{C}_{\text{OC}}$  value of marine phytodetritus in  
563 the sediment mixed layer should be around 30‰ : indeed, the  $\Delta^{14}\text{C}_{\text{OC}}$  decay of 100 years from  
564 an initial fresh marine signature of 50‰ is <15‰ (Hansman et al., 2009; Wang et al., 1998).  
565 Even taking into account the potential reservoir age of 400 years for Mediterranean marine  
566 waters (Siani et al., 2001), the large difference between the estimated ages and our  
567 radiocarbon data (Table 2) showed that most of the carbon in the Rhône River continental  
568 shelf is much older than would be expected if it had been derived from contemporarily  
569 synthesized sources (e.g., phytoplankton, vascular plants).

570 The heavily depleted values observed on the continental shelf suggested the presence  
571 of aged OC, such as kerogens, graphite, petroleum residues or black carbon (Graz et al.,  
572 2010). Originating from bedrock-derived kerogen, fossil fuels combustion or oil  
573 contamination, fossil OC generally displays a  $\Delta^{14}\text{C}_{\text{OC}}$  of around  $-1000$  ‰ (>60 kyr: it  
574 contains nearly no  $^{14}\text{C}$  (Drenzek et al., 2007; Goni et al., 2005). Indeed, high contributions of  
575 ancient carbon sources to river suspended sediments and surface shelf sediments have been  
576 observed in other RiOMar systems (Blair et al., 2003; Galy et al., 2008; Galy and Eglinton,  
577 2011; Goni et al., 2006; Gordon and Goni, 2004; Masiello and Druffel, 1998; Masiello et al.,  
578 1998). Lateral export of this aged fraction can be promoted by both selective transport of aged  
579 material sorbed onto fine particles (i.e., winnowing) and selective degradation of fresh OM  
580 along the sediment dispersal system (Hedges et al., 1999; Mannino and Harvey, 2000). As a  
581 result, the fraction of terrestrially-derived aged OM becomes gradually more important with  
582 increasing distance from river mouth.

#### 583 **5.4.1. Oil residue and pyrolytic BC as ancient OC sources**

584 As the Gulf of Lions is an intense transit area for tanker ships, we used the analysis of  
585 polycyclic aromatic hydrocarbons (PAHs) to estimate the actual contribution of fossil fuels,  
586 biomass/biofuels combustion as well as direct inputs of oil products in our sediment samples



587 (Kumata et al., 2006; Mandalakis et al., 2005; Sheesley et al., 2009; White et al., 2008; White  
588 et al., 2005). Levels of  $\Sigma\text{PAH}_6$  in the sediments of the Rhône River delta range from 450 to  
589  $600 \mu\text{g kg}^{-1} \text{ dw}$  (Table 4), yielding a total PAH concentration of  $10 \text{ mg/kg dw}$  (see result  
590 section for calculation). These levels are characteristic of present-day, chronic, intermediary  
591 contamination by PAHs of marine sediments located close to the continental loads. Oil  
592 residues represent about 30% of total PAHs in the Rhône delta (Table 4) and the remaining  
593 70% originates from fossil fuel and biomass combustion (pyrogenic origin).

594 Based on this distribution of PAHs sources, we can provide a rough estimate of ancient OC  
595 originating from petroleum and pyrogenic BC. The total oil residue-derived OC in the  
596 continental shelf sediment was estimated to be  $15 \text{ mg kg}^{-1}$  of OC i.e. 0.15% of OC whereas the  
597 pyrogenic fraction amounts to  $140 \text{ mg kg}^{-1}$ , i.e. 1.4% of total OC. A total of 1.5% of OC is  
598 found which is consistent with results of Leaute (2008) in the Thau Lagoon, a mediterranean  
599 shallow lagoon.

600 Our PAHs measurements provide us with an estimate of the pyrogenic BC and petroleum  
601 fraction of ancient OC and indicate a major contribution of oil residues and soots from vehicle  
602 combustion. The low proportion of ancient OC originating from petroleum and pyrogenic BC  
603 does not support the observed  $^{14}\text{C}$  values on the shelf. Indeed, only 2% of ancient OC mixing  
604 up with recent organic material would lead to  $\Delta^{14}\text{C}_{\text{OC}}$  values of 78‰ in the sediment, when  
605 the observed radiocarbon signatures are around -400‰ (Fig 2, Table 2). Another aged source  
606 and other processes are needed to explain the old ages of the continental shelf sediments.

#### 607 **5.4.2. Black Carbon and proto-kerogen/BC fossil OC**

608 Since the Rhône river catchment contains a lot of sedimentary rock, the depleted  $\Delta^{14}\text{C}_{\text{OC}}$   
609 values, the slightly enriched  $\delta^{13}\text{C}_{\text{OC}}$  values and the low lignin content observed in the  
610 continental shelf sediments could reflect an important contribution of kerogen-BC mixture.  
611 Indeed, as stated above, fossil OC is almost completely depleted in  $^{14}\text{C}$  and is generally

612 assumed to have a  $\Delta^{14}\text{C}_{\text{OC}}$  value of  $\sim -1000\text{‰}$  and a  $\delta^{13}\text{C}_{\text{OC}}$  signature ranging between -30 and  
613 -12‰ (Drenzek et al., 2009; Goni et al., 2005). Such  $\Delta^{14}\text{C}_{\text{OC}}$  signature is however a rough  
614 estimate since radiocarbon measurements on graphitic BC samples have shown a range of  
615 signatures from -800 to -1000‰ (Dickens et al., 2004; Drenzek et al., 2009; Drenzek et al.,  
616 2007). Likely, the rather depleted signature ( $\Delta^{14}\text{C}_{\text{OC}} \sim -400\text{‰}$ ) of continental shelf sediments  
617 indicate the presence of fossil material, probably inherited from the Rhône River material and  
618 preferentially exported along the dispersal transect.

619 As a matter of fact, our data indicate a contribution of BC to OC increasing from 12% at the  
620 river mouth to 50% on the continental shelf (Fig. 6). These values, although remarkable, are  
621 consistent with measurements carried out by Lim and Cachier (1996) in NW Mediterranean  
622 Sea. The authors, based on chemical oxidation and thermal treatments, estimated a BC/TOC  
623 ratio of 38%. The large difference between our pyrogenic BC estimates based on PAHs (1.4%  
624 of OC) and our BC measurements based on thermal oxidation (12-50% of OC) suggest a high  
625 contribution of graphite in BC. Indeed, the Thermal Oxidation method at 375°C applied here  
626 can isolate very highly condensed soot-BC and graphite but can also destroy charcoal-BC and  
627 kerogen (Elmquist et al., 2004). Therefore, the low PAH/BC ratios indicate that 90-98% of  
628 BC would be of graphitic origin. Graphitic C inputs originating from sedimentary rocks  
629 erosion occurring in the catchment of the Rhône River would thus deliver high BC fluxes and  
630 generate the high contribution of BC observed in the sediment from the prodelta and  
631 continental shelf.

632 In parallel, our data show a decrease of the proto-kerogen/BC fraction along the sediment  
633 dispersal system indicating a selective degradation of proto-kerogen like-OM as the terrestrial  
634 OM delivered by the Rhône River is exported towards the continental shelf. About 20% of  
635 proto-kerogen is lost during the export over the prodelta. Adsorption of otherwise labile  
636 organic compounds onto minerals can prevent their diagenetic degradation and promoting

637 their subsequent condensation into kerogen (Salmon et al., 2000). During the transport along  
638 the transition zone and within the prodelta sediment, selective degradation mechanisms could  
639 remove some kerogen-like material, leaving behind mineral matrix protected OM.

#### 640 **5.5. Degradation mechanisms along the sediment dispersal system**

641 A plot of  $\Delta^{14}\text{C}_{\text{OC}}$  and  $\delta^{13}\text{C}_{\text{OC}}$  values against 1/OC provides us with a mixing model taking into  
642 account changes in the bulk concentration of OC (Fig. 8). The  $\Delta^{14}\text{C}_{\text{OC}}$  and  $\delta^{13}\text{C}_{\text{OC}}$  ordinates at  
643 0.5 (max. 2% OC in the shallow prodelta during our study) indicate the loss of a modern-like  
644 OC source ( $\Delta^{14}\text{C}_{\text{OC}} \sim 59\text{‰}$ ) with a very light  $\delta^{13}\text{C}_{\text{OC}}$  terrestrial signature ( $\sim -27\text{‰}$ ) as OC  
645 decreases across the system. This loss certainly reflects the net decomposition of this  
646 terrestrial material through degradation processes and the relative accumulation of old BC  
647 offshore.

648 In this study, the lignin phenols contents of the sediments were used as another means  
649 for investigating the fate and transfer mechanisms of the terrestrial OM delivered by the river  
650 to the coastal ocean. First, a plot of S/V vs. C/V ratios (Fig. 3) indicates that angiosperm  
651 woody and leaf materials are major sources of lignin in the shallow Rhône River prodelta  
652 (station A). However, both S/V and C/V ratios gradually decrease with increasing distance  
653 from the prodelta. Variations in these two ratios are likely caused by two processes: (1)  
654 differential lignin degradation (Benner et al., 1991; Haddad et al., 1992; Hedges et al., 1988;  
655 Opsahl and Benner, 1995); and (2) differential inputs from angiosperm and gymnosperm  
656 woody and non-woody tissue (Hedges and Mann, 1979a).

657 We used lignin stable carbon isotopes to discriminate terrestrial OM between C3 and  
658 C4 plant sources. Indeed, C3 plants yield lignin phenols with  $\delta^{13}\text{C}$  values  $\leq -27\text{‰}$  while C4  
659 plants yield lignin phenols with  $\delta^{13}\text{C}$  values ranging from -13 to -19 ‰ (Goni et al., 1997). In  
660 the shallow prodelta sediments (station A), integrated lignin isotopic compositions ( $\delta^{13}\text{C}_{\text{S,V}}$ )

661 are below -30‰ (Table 3), clearly indicating a C3-plant origin. However, the  $\delta^{13}\text{C}_{\text{S,V}}$  values  
662 of the syringyl and vanillyl lignins increase by  $\sim 5\%$  from station A to station E (Table 3).  
663 The alteration of lignin  $^{13}\text{C}$  with increasing distance from the river mouth can be caused by an  
664 increase in contribution from C4-derived OM or lignin degradation. The S/V and C/V ratios  
665 indicate that gymnosperm-derived lignin accounts for a dominating fraction in off-shore  
666 sediments (Fig. 3; see above). Since no gymnosperm plants utilize the C4 photosynthetic  
667 pathway (Ehleringer et al., 1997), an increase in contribution from C4-derived OM is unlikely  
668 important for the isotopic alteration of lignins in off-shore sediments. Therefore, both lignin  
669 phenols and lignin stable carbon isotopes indicate significant lignin degradation over the  
670 transition zone.

671 Lignin is generally degraded via propyl side chain oxidation, demethylation of the  
672 methoxyl groups, and aromatic ring cleavage (Benner et al., 1991; Ertel and Hedges, 1984).  
673 Lignin-derived acid to aldehyde ratio (Ad/Al)<sub>v</sub> or (Ad/Al)<sub>s</sub> has been used as an indicator of  
674 propyl side chain oxidation (Hedges et al., 1988; Opsahl and Benner, 1995). Demethylation  
675 results in selective loss of methoxyl groups (vanillyl and syringyl phenols) but does not affect  
676 non-methoxylated phenols (p-hydroxyl phenols). Thus, the methoxylated- to non-  
677 methoxylated phenol [P/(V+S)] ratio can also be used as a diagenetic indicator of lignin  
678 (Dittmar and Lara, 2001; Dittmar et al., 2001). However, p-hydroxyl phenols are derived from  
679 a variety of lignin and non-lignin materials, limiting the applications of the [P/(V+S)] ratio.  
680 The ratio of p-hydroxyacetophenone (PON) to total p-hydroxyl phenols (PON/P) can be used  
681 as an indicator to determine the source of this phenol group (Benner et al., 1990). When  
682 aromatic ring cleavage is a dominating pathway for lignin degradation, neither (Ad/Al) nor  
683 P/(V+S) ratio can be elevated (Dittmar and Lara, 2001). Our lignin data (Table 3) show that  
684 the (PON)/P ratios remain almost constant despite a remarkable decrease of total p-hydroxyl  
685 phenols from the prodelta to the shelf, indicating that the sources of this phenol group at

686 different sampling sites are the same and the PON has a reactivity similar to total p-hydroxyl  
687 phenols decomposition. Based on this, P/(V+S) ratios can be reliably used as an indicator for  
688 lignin degradation. In fact, we observed a doubling in P/(V+S) in offshore versus river mouth  
689 sediments while little changes are observed in (Ad/Al)<sub>v</sub>, suggesting that lignin becomes  
690 increasingly degraded with off-shore transport, mainly via a demethylation pathway. In  
691 addition, there is evidence that isotopic compositions of lignin compounds can be altered  
692 during degradation processes (Bahri et al., 2008). So, the degradation of lignin along the  
693 dispersal sediment system is likely responsible for the alteration in isotopic signature of lignin  
694 that we see in the transition zone.

695 Degradation of OM in sediments from the Rhône River estuary to continental shelf  
696 has been demonstrated using different proxies. For example, two independent indexes based  
697 on amino acid (Dauwe's Index Dauwe et al., 1999) and pigments (ratio of intact chlorophyll-a  
698 to the sum of chlorophyll-a + phaeopigments) consistently indicate an increase in degradation  
699 state of OM along the transect (Pastor et al., 2011a; Bourgeois et al., 2011). The terrestrial  
700 material in Rhône River is largely composed of fresh and labile material (Cathalot et al.,  
701 2010; Pastor et al., 2011a), as indicated by the modern  $\Delta^{14}\text{C}_{\text{OC}}$  signatures observed at the river  
702 mouth, and its lability appears to drive degradation processes in the Rhône River prodelta.  
703 Indeed, the increase in degradation state of OM in the prodelta and the adjacent shelf is  
704 correlated with the decrease of both terrestrial biomarkers (fatty acids and chlorophyll-b) and  
705 benthic mineralization rates (Cathalot et al., 2010). Our radiocarbon data are significantly  
706 correlated with the Dauwe Index from Bourgeois et al (2011) ( $r^2=0.89$ ,  $p<0.005$ ), suggesting  
707 that the distribution of  $\Delta^{14}\text{C}_{\text{OC}}$  signatures is directly related to the degradation processes.

708 Changes in OM composition during the offshore transport due to selective  
709 stabilization and degradation of organic compounds can be a predominant feature in the OM  
710 cycling of RiOMar systems (Goni et al., 2005; Zonneveld et al., 2010). Our data suggest that,

711 along its dispersion offshore, the OM is selectively degraded with fresh material and proto-  
712 kerogen OM being removed through degradation processes, as evidenced by biomarkers and  
713 oxygen demand of the sediment (Bourgeois et al., 2011; Cathalot et al., 2010). The OM on the  
714 shelf corresponds to a degraded “aged” OM, which will then remain on the continental shelf  
715 and be further exported or reworked. If the input of terrestrial organic matter in this system is  
716 obvious, the proportion of marine OM is an open question.

## 717 **5.6. Inputs of fresh marine Organic Matter**

718 In addition to the selective degradation processes occurring along the main dispersal  
719 system, many studies in deltaic environments have shown that isotopic and biogeochemical  
720 characteristics of POM result from the dilution of the terrestrial material with freshly  
721 produced marine phytoplankton (Fry and Sherr, 1984; Hedges et al., 1997; Tesi et al., 2007b).  
722 To assess if such dilution processes could explain the radiocarbon signatures observed in the  
723 sediments of the Gulf of Lions continental shelf, we applied a three end-members mixing  
724 model to our Gulf of Lions sites based on isotopic composition ( $\Delta^{14}\text{C}_{\text{OC}}$ ,  $\delta^{13}\text{C}_{\text{OC}}$ ), and lignin  
725 contents ( $\Lambda_6$ ). This model has two contemporary terrestrial and marine sources, and a  
726 kerogen-BC source (Fig. 5 and 9). Marine phytoplankton, exempt of lignin, was assumed to  
727 display a  $\Delta^{14}\text{C}_{\text{OC}}$  signature following the  $\Delta^{14}\text{C}_{\text{DIC}}$  values ( $\sim 100 - 120\%$ ) of the Mediterranean  
728 Sea surface waters (Yechieli et al., 2001) and  $\delta^{13}\text{C}_{\text{OC}}$  signatures were taken from Harmelin-  
729 Vivien et al. (2008). The parameters for the two contemporary and kerogen-BC terrestrial  
730 end-members were taken from both our isotopic measurements and values from the literature.  
731 Based on these end-members, we show that sediment of the continental shelf would need a  
732 contribution of 30%, 40% and 30% of fresh terrestrial material from the Rhône River,  
733 kerogen-BC and fresh marine OM respectively (Fig. 9).

734 The mixing model clearly indicates a gradient of increasing contributions of marine  
735 OM and kerogen-BC mixture along the dispersal axis. Immediately after the transition zone,

736 the model-based contribution of kerogen-BC to OC increases from 10% in the prodelta to  
737 ~40% all over the continental shelf (station C and E): this is in good agreement with our BC  
738 data (Fig. 6) confirming that the material delivered by the Rhône River consists of fossil OC  
739 (kerogen-BC mixture) mixed with a fresh terrestrial material quickly deposited within the  
740 prodelta. The fossil OC is exported to the continental shelf, reaching 50% of OC in the Gulf  
741 of Lions.

742 Similarly, the model-based marine fraction increases along the dispersal gradient from  
743 ~10% in the prodelta up to 30% over the continental shelf. This aspect is rather surprising  
744 since many proxies in the literature show no increase in labile marine OM over the  
745 continental shelf (Bourgeois et al., 2011; Pastor et al., 2011b). In addition, primary  
746 productivity within the Rhône River plume and over the continental shelf is rather low (Conan  
747 et al., 1998; Lefevre et al., 1997), in agreement with the gradient of mineralization activity  
748 along the dispersal transect which is governed by the fresh terrestrial inputs of the Rhône  
749 River in the prodelta (Cathalot et al., 2010) rather than inputs of fresh marine OM on the  
750 continental shelf. There is a clear discrepancy between our mixing model results and the  
751 biomarkers/mineralization features evidenced in previous studies. Likely, the presence of 30%  
752 of fresh marine OM in the continental shelf sediment as predicted by the mixing model is an  
753 overestimation. Reconciling these two approaches will require a better definition of the end-  
754 members of the model (i.e. OC sources) and the processes involved along the main dispersal  
755 transect.

756

## 757 **5.7. Resuspension on the continental shelf**

758 Although the accumulation of old BC-like carbon, dilution with fresh marine OM, and the  
759 mechanism of selective degradation of fresh terrestrial OM can explain the biomarker,  
760 isotopic and the age signature of OC in the continental shelf, some puzzling factors remain in

761 the understanding of the system. The decrease of OM quality/freshness is not obvious on all  
762 biochemical markers: the Enzymatically Hydrolysable / Total Hydrolysable Amino Acids  
763 ratios (EHAA/THAA), a proxy for degradation processes in the sediment, shows little  
764 decrease along the offshore transect (Pastor et al., 2011b). Other striking features are the  
765 homogeneity of the  $\delta^{13}\text{C}_{\text{POC}}$  composition of the SPM over the entire prodelta ( $-23.7 \pm 0.6\text{‰}$ ),  
766 their depleted  $\Delta^{14}\text{C}_{\text{POC}}$  signature (apart of station A), and their similarity with continental  
767 shelf sediments (see Tables 1 and 2, and Tesi et al., 2010).

768 These observations suggest that besides selective transport and accumulation of refractory  
769 BC-type OM, other mechanisms may be active in the transition zone. Resuspension, transport  
770 and redeposition of shelf sediments, consisting in a mixture of old marine OM and BC-  
771 kerogen material originating from the Rhône River, is one possible explanation which could  
772 contribute to the rapid apparent aging of river particles observed in the River prodelta by  
773 differential mixing with deposited shelf sediment. Intense resuspension events, associated  
774 with southeasterly storms, are frequent and repeated phenomena affect the inner-shelf  
775 sediment of the Gulf of Lions (Estournel et al., 2003; Ulses et al., 2008). Recent work  
776 performed on density-fractionated sediments (Toussaint et al., accepted) show that all density  
777 fractions from sediments located on the offshore gradient evolve in a similar way. This may  
778 be an indication of homogeneous mixing between shelf particles and sediments in the  
779 transition zone.

## 780 **6. CONCLUSION**

781 This study, based on radiocarbon, stable carbon isotopes, lignin phenols, Black Carbon  
782 and PAHs analyses, brings new insights on the origin of the organic particulate material on  
783 the Mediterranean continental shelf influenced by the Rhône River. In particular,  $\Delta^{14}\text{C}_{\text{OC}}$   
784 signatures indicate an important pool of aged OC in the continental shelf. Our data indicate an



785 important contribution of BC over the continental shelf. Selective degradation mechanisms  
786 along with coarse sediment trapping in the nearshore area promote the removal of fresh  
787 terrestrial organic matter but also kerogen-like OM delivered by the Rhône River, as it is  
788 exported off the prodelta. Clearly, degradation processes of OM plays a critical role in the  
789 aging of OM on the continental shelf off the Rhône River: entangled with OM deposition  
790 patterns, oxygen exposure time and benthic mineralization efficiencies, they are the results of  
791 an intricate interplay between the OM stock and fluxes in the system. Recent marine organic  
792 matter is hardly visible in biomarkers but a mixing model based on C isotopes and lignin  
793 indicate that it may constitute a significant proportion of OM in the sediment. An alternative  
794 model would be a resuspension/deposition/degradation loop for terrestrial and marine organic  
795 matter on the continental shelf which would mix with the sediment of the transition zone  
796 contributing to the large  $\Delta^{14}\text{C}$  gradient over the area.

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800

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1145 Table 1. Summary of intermediate and bottom waters conditions in April 2007 cruise. Distance  
 1146 is reported respective to the Rhône River mouth.  
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	Stations	Lat. (°N)	Long. (°E)	Distance (km)	Depth (m)	T (°C)	SPM mg l <sup>-1</sup>	[POC] (µgC l <sup>-1</sup> )	[POC] (%)	δ <sup>13</sup> C (‰)	Δ <sup>14</sup> C (‰)		Radiocarbon ages (yr)	
<b>Prodelta area</b>	A	43° 18' 48"	4° 51' 6"	1.9	13	14.9	1.6	152.3	9.3	-23.4	29.2	+ 0.2	post-bomb	
					25	15.2	2.8	217.6	7.8	-24.1	-72.8	+ 0.1	609 :87	
	B	43° 18' 11"	4° 50' 8"	3.1	25	14.8	2.1	247.6	11.9	-21.7	-168.0	+ 0.1	1479.0 :86	
					57	14.8	5.0	207.6	4.2	-24.4	-212.8	+ 0.1	1930 :110	
	K	43° 18' 7"	4° 51' 28"	3.3	31	15.3	0.9	106.5	11.4	-24.1	-	-	-	
					63	14.8	2.9	137.2	4.8	-23.5	-	-	-	
	L	43° 18' 6"	4° 52' 48"	4.2	66	14.3	2.0	218.4	11.0	-	-	-	-	
<b>Continental shelf</b>	C	43° 16' 21"	4° 46' 44"	8.3	40	14.8	1.9	-	-	-	-	-	-	
					76	14.5	4.1	159.2	3.9	-23.8	-298.2	+ 0.1	2847 :98	
	D	43° 15' 3"	4° 43' 48"	12.8	73	14.3	2.8	152.2	5.5	-23.7	-	-	-	
	E	43° 13' 18"	4° 41' 59"	16.8	35	14.5	1.8	117.0	6.4	-23.2	-67.8	+ 0.1	561 :86	
					75	14.2	3.5	146.0	4.2	-24.4	-320.4	+ 0.1	3106 :92	
	F	43° 10' 10"	4° 39' 1"	23.8	40	14.4	1.6	120.2	7.4	-23.9	-	-	-	
					78	14.2	3.1	155.5	5.0	-24.1	-	-	-	
	G	43° 18' 30"	4° 47' 17"	5.2	47	14.8	5.0	174.3	3.5	-	-	-	-	
	H	43° 15' 54"	4° 49' 11"	7.5	40	15.1	1.3	105.5	8.3	-23.1	-	-	-	
					86	14.5	2.3	137.3	6.1					
	I	43° 15' 59"	4° 53' 0"	7.7	89	15.1	5.4	181.4	3.4	-23.8	-	-	-	
	J	43° 18' 15"	4° 58' 2"	10.3	86	14.1	1.3	105.1	7.9	-24.3	-111.8	+ 0.1	958 :92	
M	43° 9' 59"	4° 44' 4"	20.3	91	14.1	2.1	137.3	6.7	-	-	-	-		
N	43° 17' 29"	4° 48' 3"	5.6	3	15.2	2.4	265.7	11.0	-23.0	-	-	-		
				32	15.2	2.4	123.9	5.2	-23.2	-	-	-		
				67	14.5	5.2	-	-	-	-	-	-		
O	43° 16' 58"	4° 49' 44"	5.4	79	14.4	2.8	137.3	4.8	-24.4	-	-	-		
R2	43° 14' 28"	4° 52' 55"	10.3	98	14.1	0.8	77.4	9.7	-23.8	-	-	-		
<b>Rhône</b>									1.6	-27.1	147.7	+ 2.8	post-bomb	
									1.9	-27.5	77.8	+ 2.8	post-bomb	
									0.8★	-25.8★	-495.1★	+ 1.7	5510 :30	
									1.6	-27.2	40.6	+ 3.1	post-bomb	
													;	
										2.7	-26.8	-89.7	+ 2.6	757 :25
													;	
									1.6	-27.8	-37.0	+ 2.8	304 :24	

1148  
 1149 ★ indicate the June 2008 atypical flood originating from the Durance basin.  
 1150

1151 Table 2. Isotopic OC parameters from selected stations of the Rhône prodelta sediments

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	Stations	Lat. (°N)	Long. (°E)	Depth (m)	Distance (km)	Cruise	Sediment depth (cm)	C <sub>org</sub> (%)	δ <sup>13</sup> C (‰)	Δ14C (‰)	Age <sup>14</sup> C <sub>OC</sub> (yr BP)	Λ <sub>s</sub> Syringyl + Vanyllin Phenols*	δ <sup>13</sup> C <sub>Sy</sub> (‰) Syringinc + Vanillin pool
Prodelta transition area	A	43° 18' 47"	4° 51' 4"	24	1.93	Jun-05	0-1	1.81	-26.8	143 ± -14	modern	3.18 ± 0.07	-31.3
							3-4	1.92	-27.1	128 ± -14	modern	3.16 ± 0.27	-30.3
							Apr-07	0-1	1.99	-27.2	59 ± -2	modern	-
	B	43° 18' 14"	4° 50' 4"	54	3.02	Jun-05	0-1	1.68	-26.7	13 ± -14	modern	-	-
							3-4	1.55	-26.7	53 ± -13	modern	-	-
							Apr-07	0-1	1.61	-26.6	7 ± -3	modern	-
	K	43° 18' 7"	4° 51' 29"	62	3.28	Jun-05	0-1	1.18	-26.2	-8 ± -14	65	-	-
							3-4	1.10	-26.2	-80 ± -13	675	-	-
							Apr-07	0-1	1.79	-26.7	-	-	-
	L	43° 18' 24"	4° 52' 59"	62	4.03	Jun-05	0-1	1.15	-25.9	-121 ± -10	1035	-	-
							3-4	1.28	-26.0	-102 ± -10	865	-	-
							Apr-07	0-1	1.51	-26.3	-	-	-
Continental shelf	C	43° 16' 17"	4° 46' 33"	76	8.57	Jun-05	0-1	1.02	-25.3	-218 ± -9	1980	1.76 ± 0.07	-28.1
							3-4	1.03	-25.3	-222 ± -8	2025	1.49 ± 0.14	-29.7
							Apr-07	0-1	1.25	-25.4	-226 ± -2	2075	-
	D	43° 14' 54"	4° 43' 46"	74	13.01	Jun-05	0-1	0.93	-24.5	-263 ± -8	2450	-	-
							3-4	0.93	-24.7	-255 ± -8	2365	-	-
							Apr-07	0-1	1.05	-24.8	-	-	-
	E	43° 13' 12"	4° 41' 54"	75	17.03	Jun-05	0-1	0.89	-24.3	-312 ± -7	3010	0.32 ± 0.06	-27
							3-4	0.90	-24.3	-319 ± -7	3095	0.31 ± -	-23
							Apr-07	0-1	-	-24.5	-	-	-
	F	43° 10' 1"	4° 41' 59"	78	21.61	Jun-05	0-1	-	-	-	-	-	-
							3-4	-	-	-	-	-	-
							Apr-07	0-1	1.43	-24.2	-400 ± -4	4120	-
	H	43° 15' 53"	4° 49' 10"	86	7.52	Jun-05	0-1	1.03	-25.2	-217 ± -8	1965	-	-
							3-4	1.03	-25.5	-249 ± -7	2305	-	-
							Apr-07	0-1	1.17	-25.6	-	-	-
	I	43° 16' 0"	4° 53' 1"	89	7.68	Jun-05	0-1	0.82	-24.3	-115 ± -11	980	-	-
							3-4	0.88	-24.5	-330 ± -7	3215	-	-
							Apr-07	0-1	1.03	-25.1	-	-	-
	J	43° 16' 7"	4° 58' 6"	86	12.09	Jun-05	0-1	0.82	-23.9	-386 ± -6	3925	-	-
							3-4	0.97	-24.1	-393 ± -6	4010	-	-
							Apr-07	0-1	-	-	-	-	-
	N	43° 17' 33"	4° 47' 59"	67	5.54	Jun-05	0-1	-	-	-	-	-	-
							3-4	-	-	-	-	-	-
							Apr-07	0-1	1.43	-25.9	-	-	-
O	43° 17' 0"	4° 50' 6"	79	5.22	Jun-05	0-1	-	-	-	-	-	-	
						3-4	-	-	-	-	-	-	
						Apr-07	0-1	1.43	-25.7	-	-	-	-
H30	43° 18' 42"	4° 49' 34"	30	2.55		0-1	1.67	-27	-199		2.7 <sup>†</sup>	-	
SO66	43° 18' 32"	4° 30' 31"	67	29.59		0-1	0.89	-23.9	-358		0.6 <sup>†</sup>	-	
SK63	43° 20' 4"	4° 6' 19"	65	59.82		0-1	0.81	-23.3	-412			-	
SC63	43° 0' 31"	3° 19' 21"	64	128.54		0-1	0.83	-22.9	-399			-	

1153

1154 The error in AgeOC is ± 30 years for all samples.

1155 \* Units: mg/100mgOC. Sum of vanillyl + syringyl phenol yields ( $\Lambda_6$ ) was calculated by  
1156 excluding cinnamyl phenols to compare directly to previous data (Sheesley et al, 2009)

1157 † Sum of vanillyl + syringyl + cinnamyl phenol yields ( $\Lambda_8$ ) (Tesi et al, 2007)

1158

1159 Table 3: Composition of lignin parameters obtained in April 2007 from selected stations of the Rhône prodelta and adjacent continental shelf  
 1160 sediments

Stations	Sediment depth (cm)	S*	V*	C*	P*		PON/P		S/V		C/V		(Ad/Al) <sub>v</sub>		P/(S+V)	
		<i>Syringyl Phenols</i>	<i>Vanillin Phenols</i>	<i>Cinnamyl Phenols</i>	<i>p-hydroxyl Phenols</i>		<i>PON/p-hydroxyl ratio</i>	<i>Syringyl/Vanillin ratio</i>	<i>Cinnamyl/Vanillin ratio</i>	<i>Vanillin acid/aldehyde ratio</i>						
A	1-2	1.40 ± 0.10	1.77 ± 0.03	0.20 ± 0.03	2.13 ± 0.05	0.042 ± 0.018	0.79 ± 0.07	0.11 ± 0.02	0.32 ± 0.04	0.67 ± 0.04						
	3-4	1.41 ± 0.25	1.75 ± 0.01	0.23 ± 0.00	1.63 ± 0.18	0.049 ± 0.000	0.81 ± 0.14	0.13 ± 0.00	0.31 ± 0.05	0.52 ± 0.12						
C	1-2	0.45 ± 0.09	1.31 ± 0.02	0.23 ± 0.05	1.87 ± 0.14	0.031 ± 0.018	0.35 ± 0.07	0.18 ± 0.03	0.43 ± 0.05	1.06 ± 0.15						
	3-4	0.48 ± 0.07	1.01 ± 0.06	0.12 ± 0.06	1.52 ± 0.07	0.027 ± 0.003	0.47 ± 0.05	0.12 ± 0.06	0.28 ± 0.33	1.02 ± 0.03						
E	1-2	0.09 ± 0.02	0.23 ± 0.03	0.02 ± 0.01	0.38 ± 0.02	0.037 ± 0.004	0.40 ± 0.04	0.07 ± 0.03	0.37 ± 0.12	1.17 ± 0.10						
	3-4	0.08 ± -	0.23 ± -	0.02 ± -	0.31 ± -	0.048 ± -	0.36 ± -	0.08 ± -	0.29 ± -	1.00 ± -						
		$\delta^{13}C_{S,V}$ (‰)	$\delta^{13}C_{SI}$ (‰)	$\delta^{13}C_{Sd}$ (‰)	$\delta^{13}C_{Sn}$ (‰)	$\delta^{13}C_{VI}$ (‰)	$\delta^{13}C_{Vn}$ (‰)	$\delta^{13}C_{Vd}$ (‰)	$\delta^{13}C_{pC}$ (‰)							
		<i>Syringinc+Vanillin pool</i>	<i>Syringaldehyde</i>	<i>Syringic Acid</i>	<i>Acetosyringone</i>	<i>Vanillin</i>	<i>Acetovanillone</i>	<i>Vanillic Acid</i>	<i>p-Coumaric Acid</i>							
A	1-2	-31.3 ± 0.5	-28.7 ± 1.8	-39.9 ± 1.4	-31.3 ± 0.8	-29.9 ± 0.3	-29.1 ± 0.8	-38.7 ± 0.5	-32.8							
	3-4	-30.3 ± 0.3	-30.4 ± 0.4	-34.4 ± 1.7	-30.1 ± 0.6	-28.5 ± 0.7	-28.2 ± 0.6	-35.6 ± 0.8	-30.8							
C	1-2	-28.1 ± 0.5	-24.1 ± -	-32.5 ± 2.3	-32.8 ± 1.6	-26.2 ± 0.1	-29.0 ± 3.6	-32.2 ± 1.3								
	3-4	-29.7 ± 0.8	-27.5 ± 2.5	-29.2 ± 0.2	-33.2 ± 2.1	-28.7 ± 1.1	-28.3 ± 2.8	-36.8 ± 1.3								
E	1-2	-27.0 ± 0.8	-21.9 ± -	-29.1 ± 2.9	-24.5 ± 2.5	-27.9 ± 1.3	-32.1 ± 4.2	-27.0 ± 0.7								
	3-4	-23.0 ± 1.4	-13.9 ± 5.6	-30.1 ± -	-30.9 ± 3.7	-18.0 ± 2.0	-28.7 ± 0.6	-39.6 ± 3.8								

1162

1163

1164 \* units: mg/100mgOC

1165 Sum of vanillyl + syringyl phenol yields ( $\Lambda_6$ ) was calculated by excluding cinnamyl phenols to compare directly to previous data (Tesi et al,  
1166 2007).

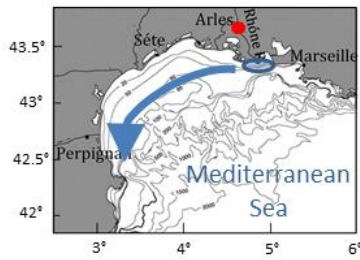
1167 Several compounds were used as internal standards for lignin oxidation, extraction, and analysis. Based off ethyl vanillin, the precision is  
1168  $\pm 0.84\%$ . It is greater for the other internal standards:  $3.50\%$  for cinnamic acid, and  $1.77\%$  for 3,4-dihydroxybenzoic acid. Ethyl vanillin and  
1169 cinnamic acid both experience the full extraction method and derivitization, whereas 3,4-dihydroxybenzoic acid only experiences derivitization.  
1170 Hence, 3,4-dihydroxybenzoic acid is most likely to be the most representative of instrumental variability

Table 4. PAH concentrations ( $\mu\text{g}/\text{kg}$  d.w.) in the Rhône delta sediments.

Station	A	C	RHO 0*	RHO 1*
Lat. N	43°18.829N	43°16.286N	43°13.903N	43°13.903N
Long. E	04°51.145E	04°46.474E	04°50.457E	04°50.457E
Depth (m)	20	75	98	98
Sampling date	2005	2005	2008	2008
Layer (cm)	1-2	1-2	0-1	1-2
% OC (dw)	1.81	1.02	0.72	0.72
PAH total ( $\mu\text{g}/\text{kg}$ d.w.)	2026.0	2074.0	2278.7	2360.4
$\Sigma\text{PAH}_6$ ( $\mu\text{g}/\text{kg}$ d.w.)	501.0	447.3	554.0	598.2
PAH (parent; $\mu\text{g}/\text{kg}$ d.w.)	935.4	878.3	1055.1	1133.2
Petrogenic component (%)	28.6	31.6	30.1	29.3

\* Continental shelf surface sediments - Rhosos cruise 2008, station KS30.

$\Sigma\text{PAH}_6$  is the summed concentrations of six indicator compounds: fluoranthene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, benzo[*ghi*]perlyene and indeno[123-*cd*]pyrene.



● Monitoring station

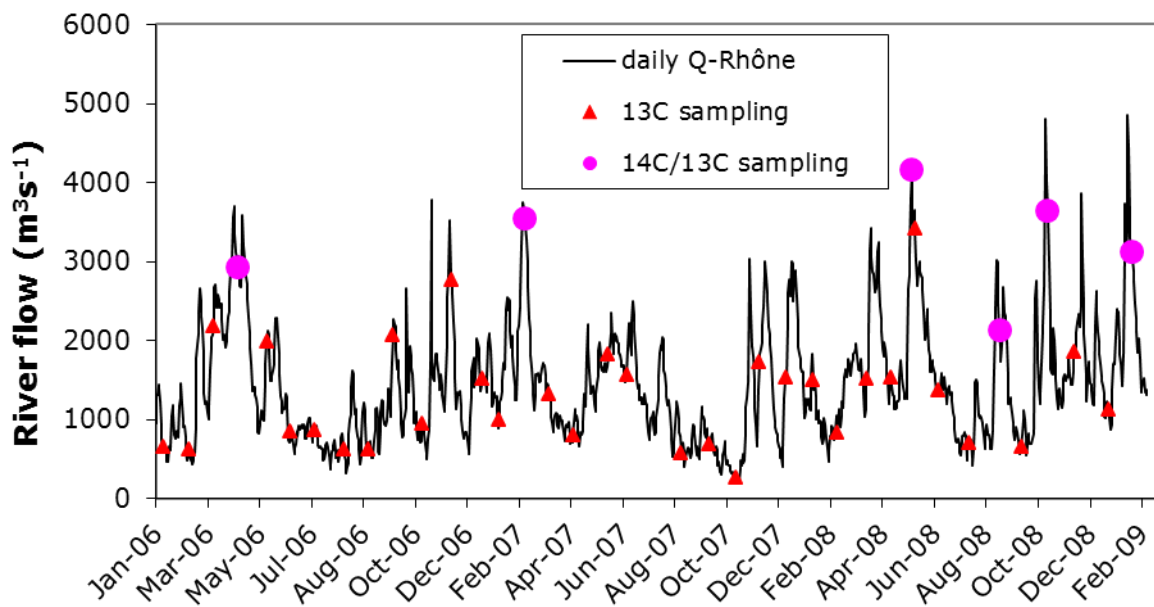
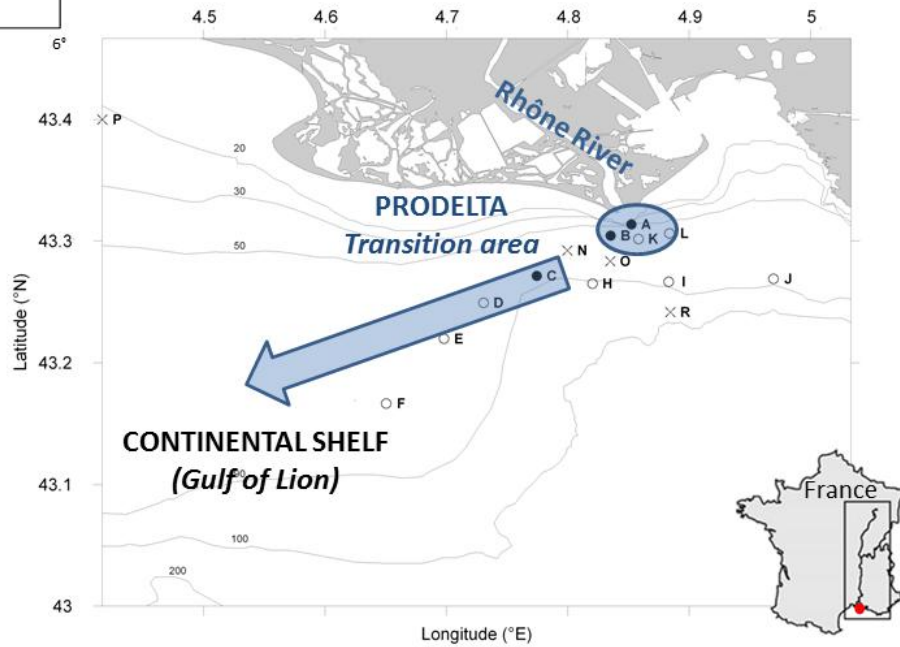


Figure 1.

Top panel. Map of the Rhône River prodelta indicating the locations of sampling stations, the main deposit entities and the main circulation direction. Circles indicate sampling stations for  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  ( $\delta^{13}\text{C}$  measured during both cruises). Filled symbols indicate that stations were sampled for  $\Delta^{14}\text{C}$  at both cruises. Crosses indicate stations sampled only for  $\delta^{13}\text{C}$  and just once (April 2007 cruise). The arrow represents the main dispersal system direction.

Bottom panel. Rhône River discharge rates between 2006 and 2009. Sampling points for  $\delta^{13}\text{C}_{\text{POC}}$  (triangles) and  $\Delta^{14}\text{C}_{\text{POC}}$  (diamond) in riverine SPM (Arles monitoring station) are also indicated.



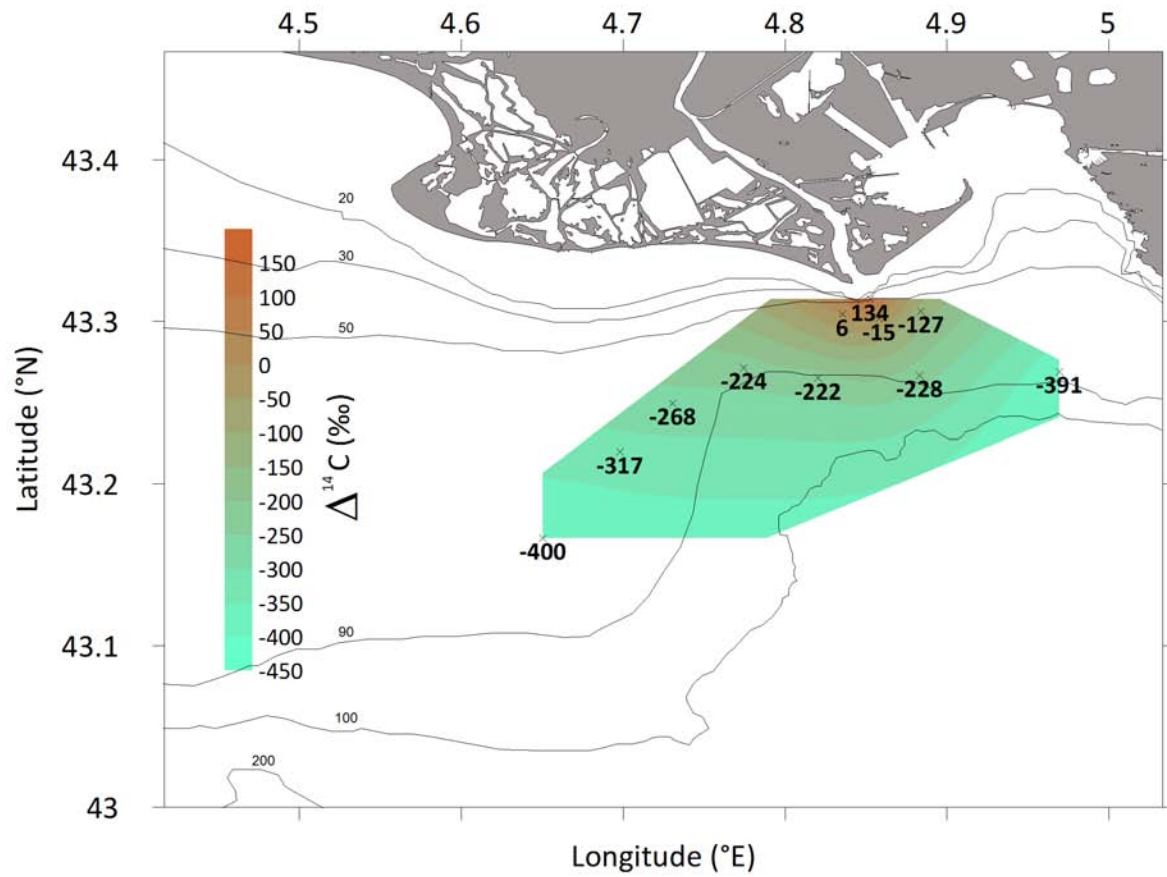


Figure 2. Spatial distribution of  $\Delta^{14}\text{C}_{\text{OC}}$  in the Rhône River prodelta. Values close to 150 ‰ correspond to terrestrial enriched material whereas -400 ‰ indicates continental shelf old material.

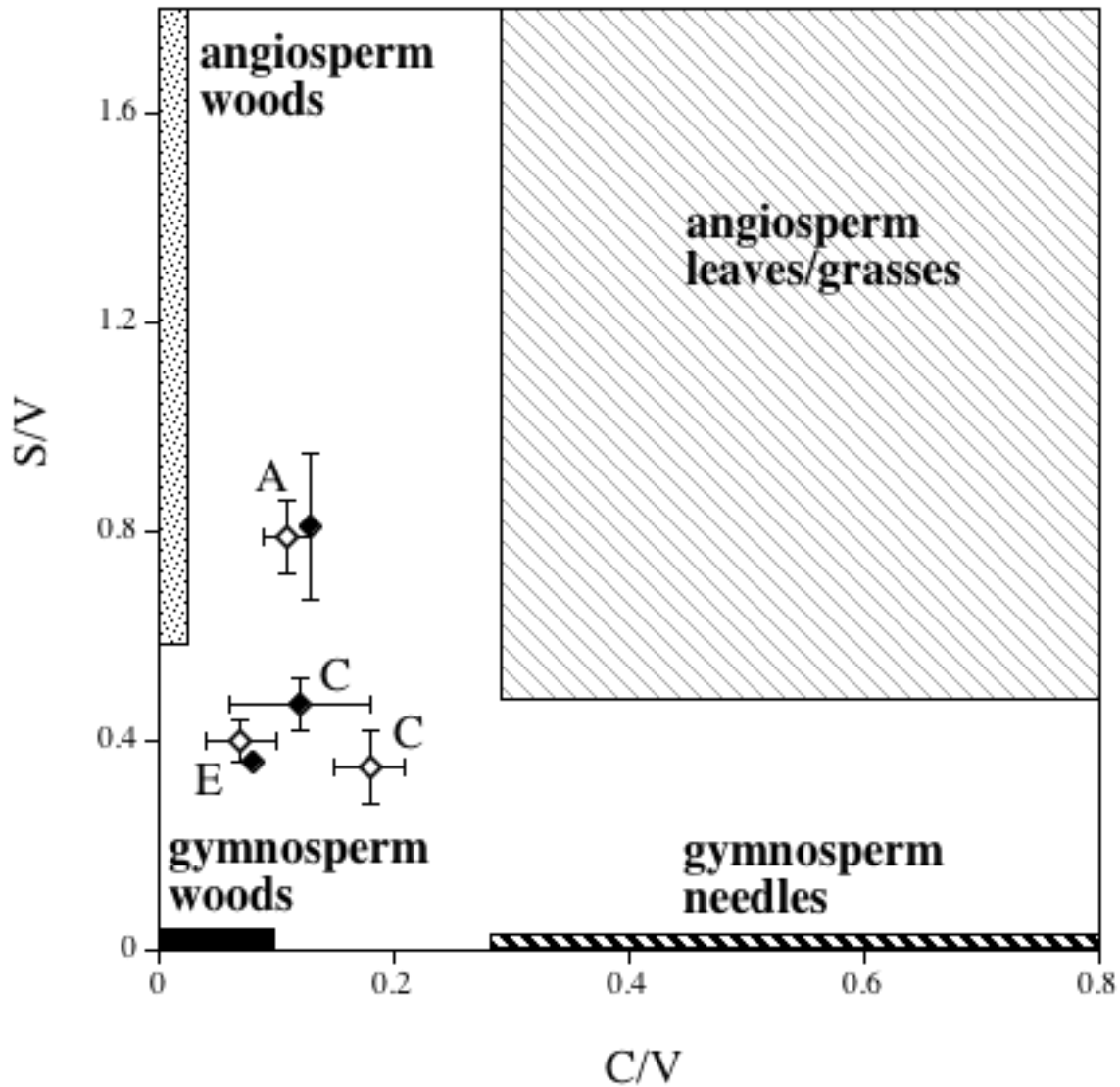
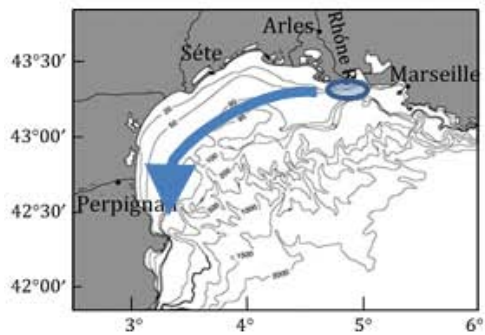


Figure 3. Plot of cinnamyl:vanillyl (C/V) vs. syringyl:vanillyl (S/V) phenol ratios for Rhône River sediments. Typical ranges for angiosperm and gymnosperm woody and non-woody tissue are indicated (Hedges and Mann, 1979; Goñi and Hedges, 1992). Open symbols represent the 1-2 cm sediment layer, and the filled symbols represent the 3-4 cm sediment layer. Stations are denoted by letter.



- this study
- Tesi et al (2007; 2010a,b)

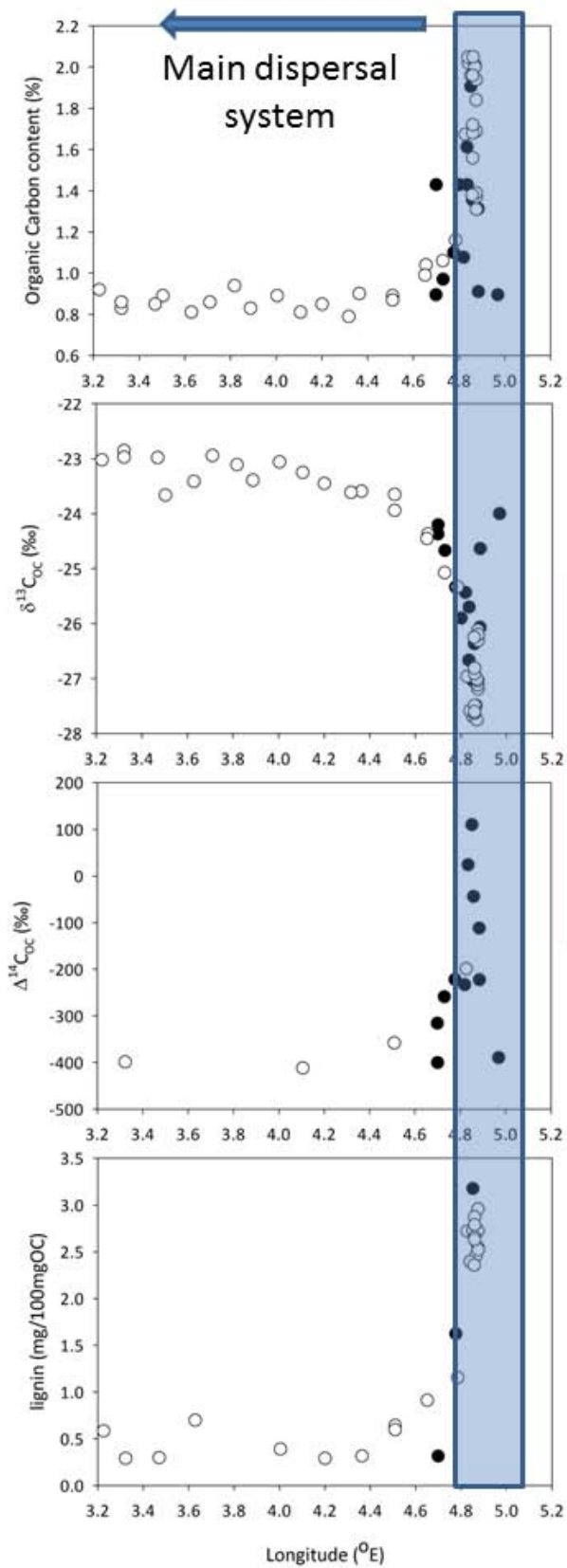


Figure 4. Biogeochemical parameters for surface sediment along the main dispersal system. The prodelta is highlighted as a transition zone for main biogeochemical characteristics. The continental shelf displays homogeneous values.

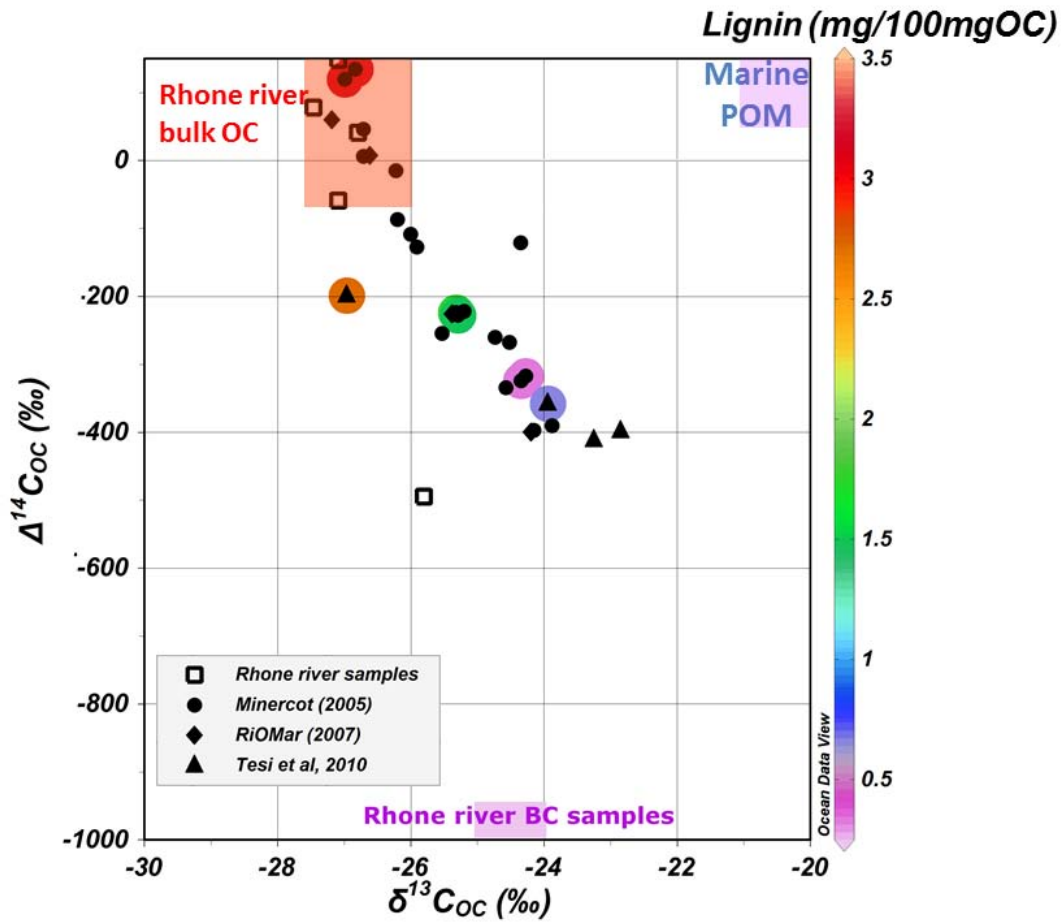


Figure 5.  $\delta^{13}C_{OC}$  -  $\Delta^{14}C_{OC}$  mixing plot with the Rhône River end-members (bulk and black carbon (BC)) plotted.

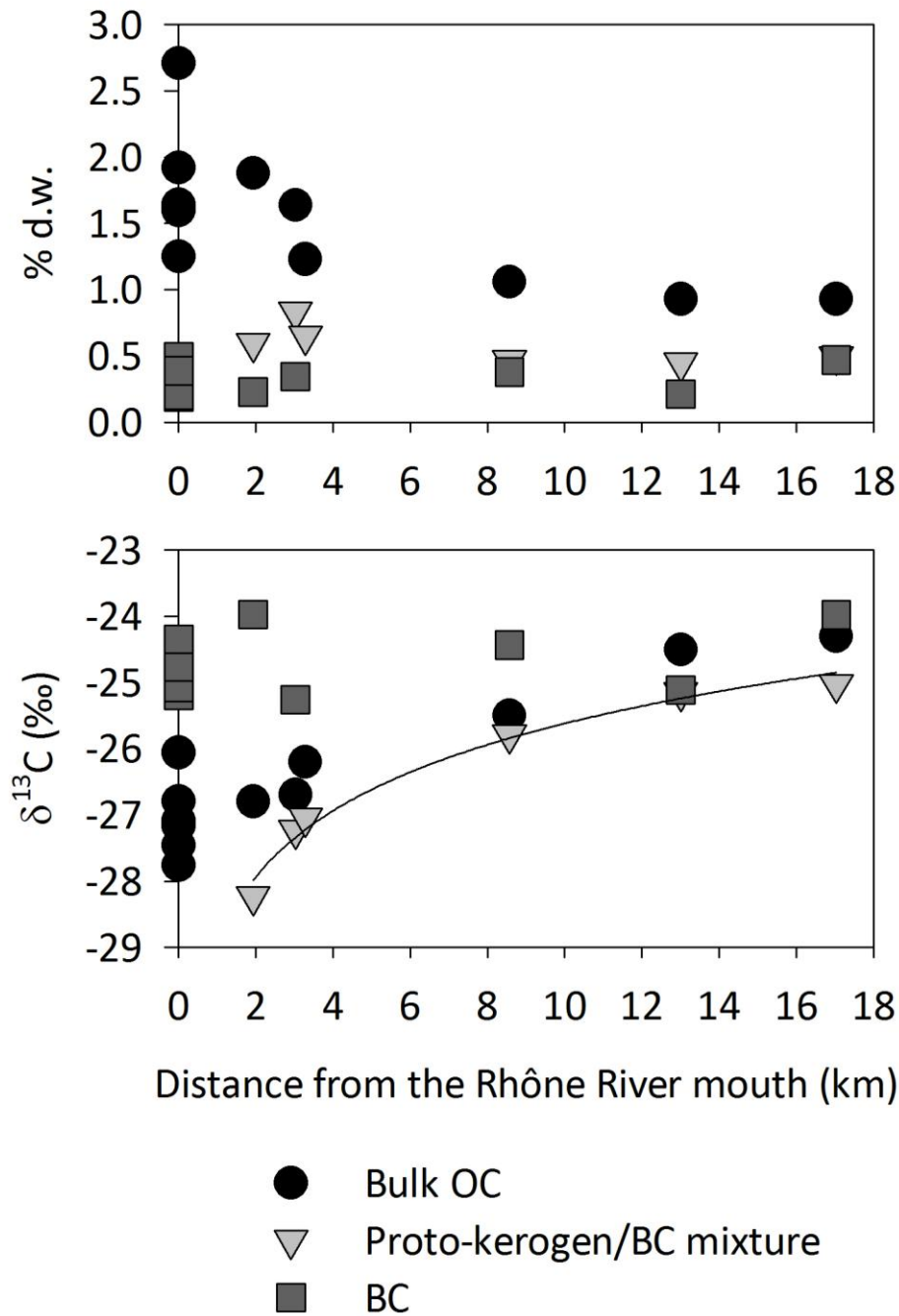


Figure 6. Bulk organic carbon (OC), black carbon (BC) and proto-kerogen/BC mixture contents (top) and respective  $\delta^{13}\text{C}_{\text{OC}}$  signatures (bottom) in the Rhône River Suspended Particulate Matter and in the prodelta sediment. The regression line in the bottom panel indicate the trend for the proto-kerogen/BC mixture in the sediment as a function of distance with the river mouth.

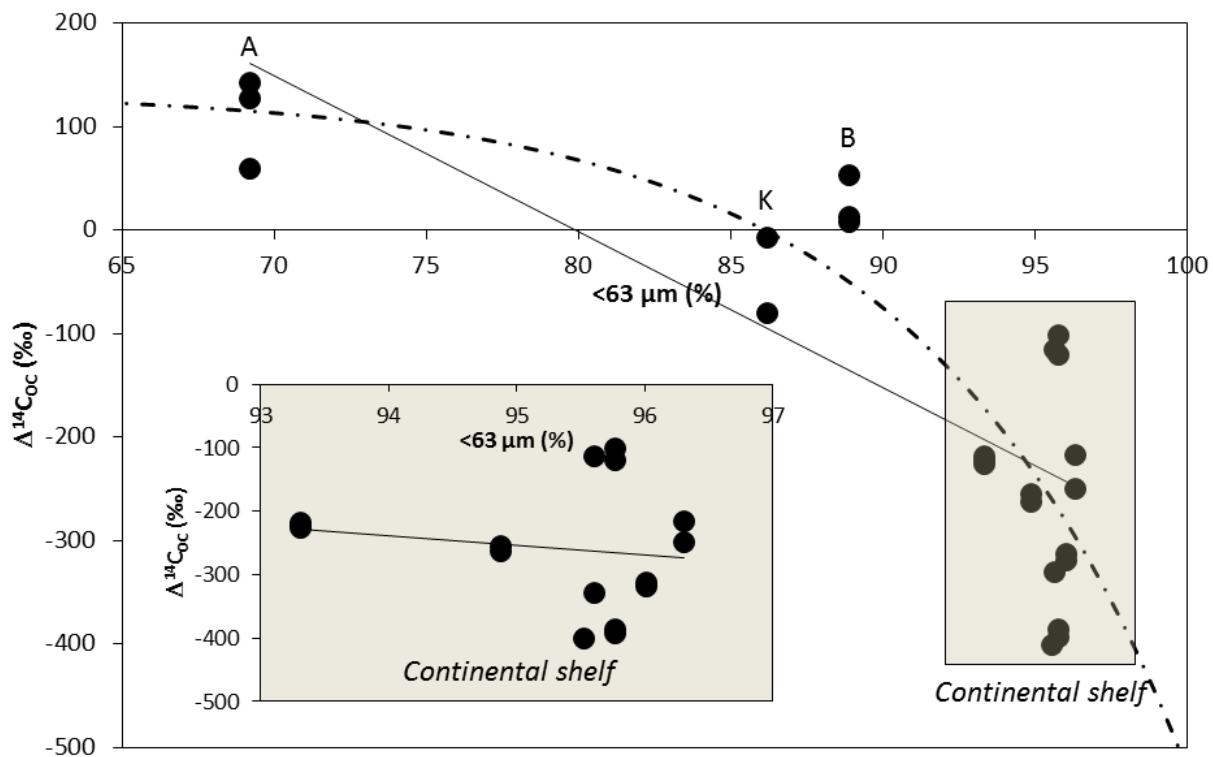


Figure 7.  $\Delta^{14}\text{C}_{\text{OC}}$  - sand content correlation (%). The dashed line represents the exponential decay fit to the data. Stations A, B and K from the prodelta are indicated. Plain line figures the linear regression.

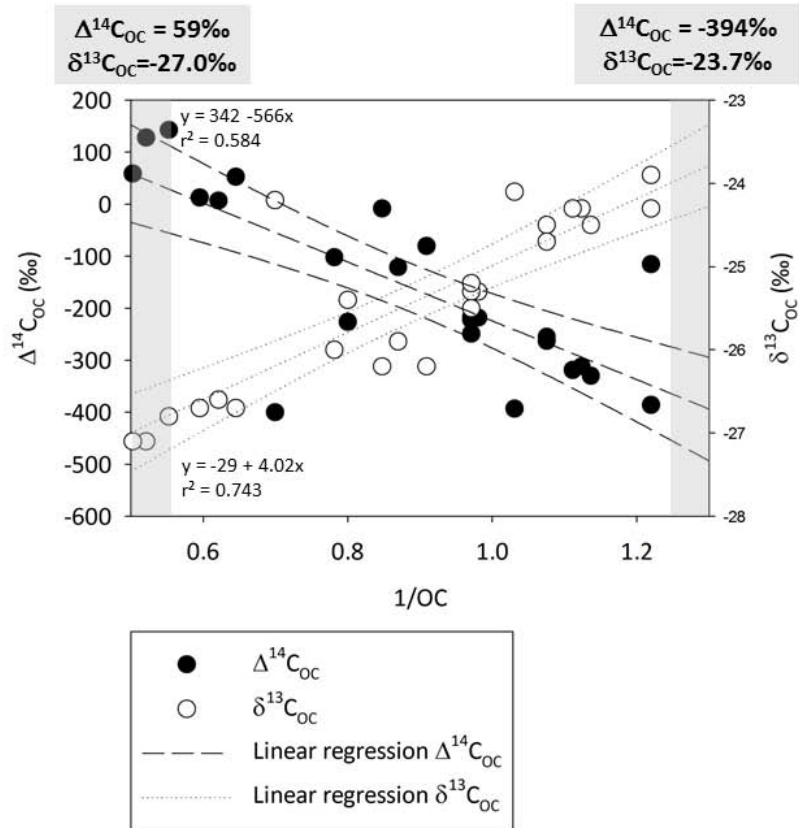


Figure 8. Mixing model of  $\Delta^{14}\text{C}_{\text{OC}}$  (●) and  $\delta^{13}\text{C}_{\text{OC}}$  (○) vs.  $1/\text{OC}$ . Net loss of terrestrial modern material as OC decrease in the system is indicated by the linear regression lines (dashed – dot for  $\Delta^{14}\text{C}_{\text{OC}}$ , and short dashed for  $\delta^{13}\text{C}_{\text{OC}}$ ). Both the linear regression fit and its 95% confidence interval are represented.



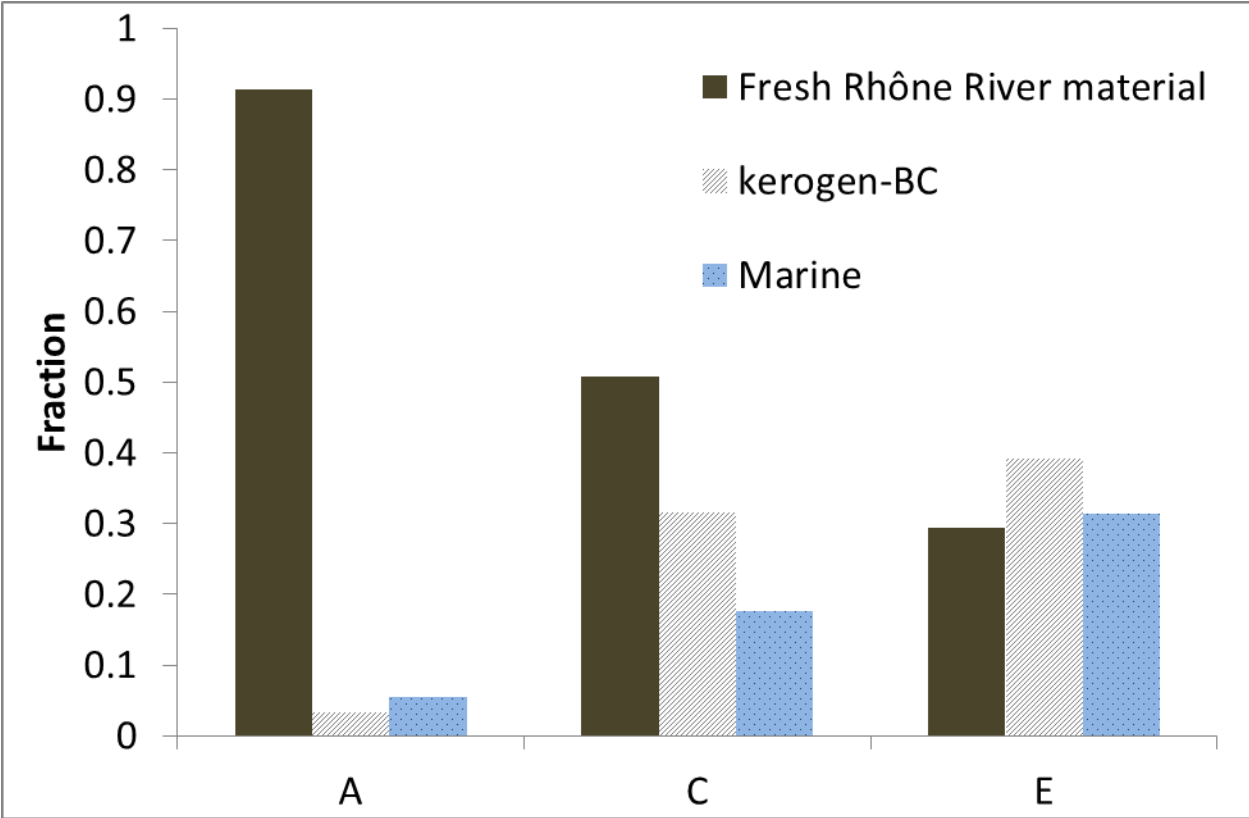


Fig. 9. Results of the mixing model considering 3 end-members: fresh terrestrial material from the Rhône River, a freshly produced marine phytoplankton (referred as marine) and a terrestrial mixture of kerogen-BC material (referred as kerogen-BC). Contributions are reported as fraction of OC.